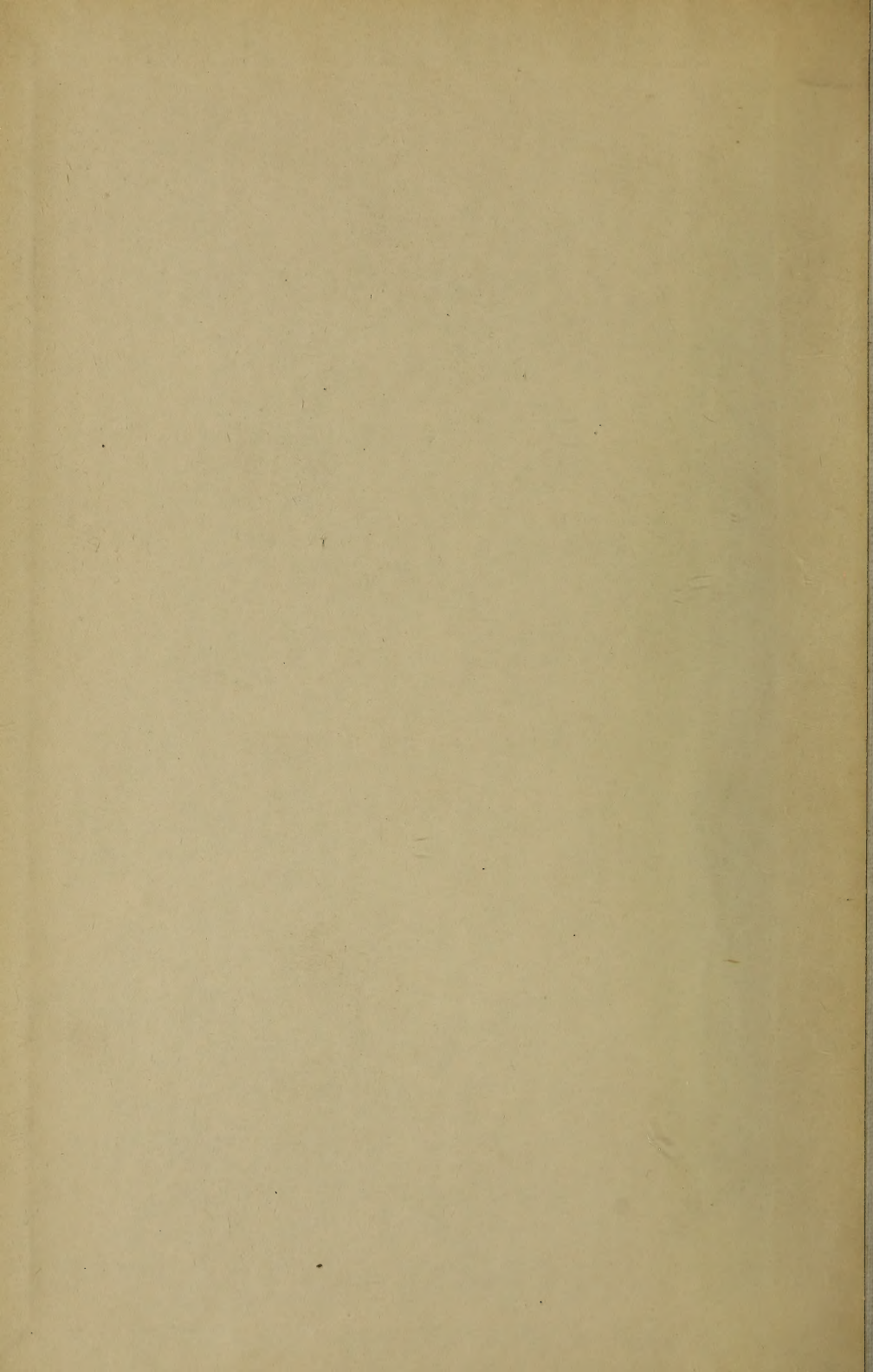


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THE SYNTHESIS OF AMMONIA

By J. W. SCOTT, B.A.Sc.

Ammonia is found widely distributed in nature. It occurs in the atmosphere forming a small but essential constituent of the air; likewise in many soils, sea clays, marls, ochres, in almost all plants, in the excrements of many animals and among the products of decay of nitrogenous organic bodies. It is also found in combination with acids as a salt in many parts of the world, deposited on the sides, the crater, crevices and in the lava of active volcanoes, in rain water and in the fumaroles of Tuscany.

The word "ammonia" occurs in two entirely different meanings. With one of these, the "gum ammoniac," we will not deal here. The other meaning of "Ammoniakon" or "Sal Ammoniacum" is that which we now connect with the word "Salammoniac." The word "ammoniakon" occurs in the first meaning already in the writings ascribed to Hippocrates, and dating from the fifth century before Christ; also in those of Pliny, Dioscorides, and other authors of the classical times, as well as later on in the writings of mediaeval Arabians and Europeans. Herodotus speaks of "hals ammoniakos," but he evidently means the crystallized rock salt (sodium chloride) of the Ammonian Oasis, and so do all the following Greek and the later Syrian and Arabian authors, up to the sixth century of our era.

In the second meaning, that which we give to the word "sal ammoniac," we find that word in Pliny, who rather indistinctly speaks of it as sometimes occurring in Egyptian "nitron" (natural soda). A more accurate knowledge of it dates only from the development of the process of sublimation and distillation in Egypt, say, about the fourth century after Christ, since it was evidently observed when burning camel dung in fireplaces provided with a chimney. The Arabian polyhistor Al-Gariz mentioned sal-ammoniac as one of the matters well known to have been obtained by the Arabs from the Greeks, by the Persian name "nashadir," which is found in various other Arabian and Persian authors later on.

Ammonia was known to the early alchemists in the form of the carbonate under the name of "spiritus salis urinae." In the

1 "Roßcol and Schorlemmer"—Treatise on Chemistry.

fifteenth century it was known that the same body might be obtained by the action of an alkali upon sal-ammoniac, and Glauber, in consequence, termed this body "spiritus volatilis salis armoniac." Sal-ammoniac which was known to the Latin Geber, appears to have been brought in the seventh century from Asia to Europe, and was known under the name of "sal-armoniacum." In later times sal-ammoniac was brought into Europe from Egypt where it was prepared from the soot obtained by burning camel's dung. Its original name was altered to "sal-ammoniacum." This last name served originally among the Alexandrian alchemists to describe the common salt and native sodium carbonate, which were found in the Libyan desert in the neighborhood of the ruins of the temple of Jupiter Ammon. Later on sal-ammoniac was obtained by the dry distillation of animal refuse such as hoofs, bones and horns; the carbonate of ammonia thus formed being neutralized with hydrochloric acid. From this mode of preparation ammonia was formerly termed "spirits of hartshorn."

Up to the time of Priestly ammonia was known only in the state of aqueous solution termed "spirits of hartshorn" or "spiritus volatilis salis ammoniac." Hales in 1727 observed that when sal-ammoniac is heated with lime in a vessel closed by water, no air is given out, but, on the contrary, water is drawn into the apparatus; Priestly in 1774, repeated this experiment, with the difference, however, that he used mercury to close his apparatus. He thus discovered ammoniac gas to which he gave the name "alkaline air." He also found that when electric sparks are allowed to pass through his alkaline air, its volume undergoes a remarkable change, and the residual air was found to be combustible. Berthollet following up this discovery in 1785, showed that the increase of volume which the ammonia gas thus undergoes is due to the fact that it is decomposed by the electric spark into hydrogen and nitrogen. This discovery was confirmed and the composition of the gas more accurately determined by Austin (1788) Davy (1800) and Henry (1809). It was shown by them, that in the reaction above described, two volumes of ammonia are resolved into three volumes of hydrogen and one of nitrogen.

The chief sources of ammonia are: The distillation of coal for gas or coke, of bituminous shales and of bones and other animal matter; putrid urine; the residues of the beet sugar industry and those left after the fermentation of molasses for alcohol; and the waste gases from blast furnaces.

At the present day almost all the ammonia and its salts are prepared from the ammoniacal liquor which is obtained as a by-product in the manufacture of coal-gas. Coal, as we know, consists of the remains of an ancient vegetable world, and contains about two per cent. of nitrogen, the greater part of which, in the process of the dry distillation of the coal carried on in the manufacture of the gas, is obtained in the form of ammonia dissolved in water along with other products formed at the same time. Chief among which are ammonium carbonate, sulphide, sulphite, sulphate, thiosulphate,

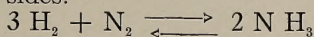
sulphocyanide and ferrocyanide. This aqueous solution is then distilled with lime and the free ammonia obtained.

On account of the great technical value of ammonia and because nitrogen compounds are an essential constituent of all living matter, various attempts have been made at synthesising ammonia.

Probably the first man to attempt this synthesis was Donkin, who attempted to produce ammonia by passing an electric spark through a mixture of three volumes of hydrogen and one volume of nitrogen. This process is unsuccessful due to the small yield of ammonia obtained, as 94-98% of the ammonia formed is decomposed back into its elements and only 2-6% union of the constituents occur under the same circumstances. This is due to the heat formed by the electric spark.

The ammonia equilibrium is attracting much attention at the present day, as several well known chemists are still investigating this problem.

F. Haber and G. Vanoordt,¹ who have been interested in this problem have done some splendid work upon it. A current of pure ammonia was led over finely divided iron kept at a temperature near 1000°C. The decomposition products were freed from the undecomposed ammonia by leading them through standard acid, then led over a further quantity of finely divided iron and the amount of ammonia reformed was determined. The iron was prepared from iron oxalate in a current of ammonia and was supported on asbestos in the heating tube. Some experiments were also made with fairly divided nickel supported on silicic acid with nickel nitrate and igniting in a current of hydrogen, but the metal proved a less effective catalyst than iron. The results obtained show that equilibrium is attained from both sides.



Exp.	Catalyst.	Residual gas at 0° & 760 mm. consisting of N ₂ & 3H ₂ liters.	Parts of ammonia decomposed per 1000	Parts of ammonia formed per 1000	Temp.
1	Iron	14.509	← .08 →		1057 + or - 23 (*)
2	"	17.948	← .46 →		1037 + or - 17
3	"	15.706	.20	.26	1029 + or - 19 (- 10)
4	"	16.530	.21	.14	1010 + or - 10 (+ 15)
5	"	13.786	.23	.16	1009 + or - 6 (- 4)
6	"	16.863	.15	.14	1016 + or - 4 (+ 9)
7	"	11.380	.20	.21	1013 + or - 17
8	Nickel	12.173	.25	.11	1024 + or - 18
9	"	12.359	.485	.272	1020 + or - 4

* Lower temp. at the beginning of Exp.

In experiments 1, 2, 8 and 9, the two tubes containing the catalyst were arranged in the same heating tube, but in experiments 3, 4, 5, 6 and 7, two heating tubes were used. The figures in the brackets give the variation of the temp. of the second tube from that of the first.

From the results of experiments, Haber and Vanoordt have calculated the free energy of the formation of ammonia and have

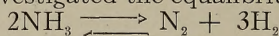
¹ Z. Anorg. Chem. 1905 or J. Soc. Chem. Ind. 1905.

deduced the following values for the amounts of ammonia contained in mixtures of N_2 , H_2 and NH_3 in equilibrium at 760 mm. pressure and temperatures given.

27°C	- 98.51%
327°C	- 8.72%
627°C	- .21%
927°C	- .024%
1020°C	- .012%

These figures show that in the synthesis of ammonia in order to obtain results of technical value, a catalyst is needed which will act satisfactorily at a temperature not much above 300°C.

Haber and a student of his, R. LeRossignol,¹ pursued this question further. They investigated the equilibrium



at various temperatures in continuation of previous experiments at 1000°. The method consisted in passing dried ammonia through quartz or glazed porcelain tubes heated in an electric furnace. The temperature was measured by means of a thermo-element. As catalysing agents metallic iron, nickel, chromium and manganese were used. The gases were passed through standard hydrochloric acid and the unchanged ammonia determined by titration. The unabsorbed hydrogen and nitrogen were then passed through a second tube, where a reverse action occurred. The newly formed ammonia was determined as before. The residual hydrogen and nitrogen were measured and samples analysed. The equilibrium constant from the expression

$$\frac{P_{NH_3}}{P_{N_2} \times P_{H_2}^3} = K_p$$

was determined for the following temperatures:

Temp.	$10^4 K_p$
1000	1.48
930	2.0
850	2.79
800	3.34
750	4.68
700	6.8

The ratio of unchanged ammonia to ammonia taken, was somewhat less at 1000°C than Haber and Van oordt previously found, and totalled from 1.1 to 2.5 ten-thousandths. The position of equilibrium was not so greatly altered by lower temperatures, as had been calculated from Haber and Vanoordt's experiments.

$$\text{Nernst's expression, } \log K_p = \frac{12000}{4.571T} - 175 \log T - 1.3$$

1. Chem. Abstracts, 1907.

may be altered to agree well with the experimental results by adding to the right hand side a member derived from the mean specific heat of ammonia under constant pressure.

Due to a disagreement between Haber and Nernst, as to the relative concentrations of the reacting gases at the point of equilibrium, Nernst maintaining that at atmospheric pressure the amount of ammonia is too small to be accurately determined, Haber and LeRossignol have performed a large number of experiments employing pressures of thirty atmospheres. The equilibrium was reached from both sides. The results obtained at thirty atmospheres pressure are in full accordance with those previously obtained at one atmosphere. The reaction tube consists of transparent quartz. Up to temperatures of 1000° the loss due to diffusion of the gases through the walls of the tube was negligible. The catalyser was finely divided iron or manganese. At 901°C and 30 atmos. the equilibrium value for the concentration of ammonia was found to be .206% by volume, a mean value of a large number of determinations. At 801° and under the same pressure .334% ammonia was found and at 700° .65% ammonia. In all of the experiments the original gas consisted of either ammonia or wholly dissociated ammonia or a mixture of three volumes of hydrogen and one of nitrogen. The results are not in harmony with those of Nernst.

Nernst disagreed with Haber over the equilibrium of the reaction $\text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3$ consequently the equilibrium was investigated anew. According to the reaction $2\text{NH}_3 \rightarrow 3\text{H}_2 + \text{N}_2$, high pressure will tend to increase the output in ammonia. A porcelain tube furnace incased in an iron pipe was used and pressures of 12 to 70 atmospheres were applied. The reaction gases were passed over platinum foil, which acted as catalyser, and from the further end of the tube passed through a fine porcelain capillary. The speed of the gas mixture could be regulated at will. The temperature ranged between 685° and 1040° . The ammonia content was determined by analysis. The experimental values agree very well with the theoretical. The heat of reaction Q (for 2NH_3) was found to be 28020 cals. a value somewhat higher than that determined by Thomson or Berthelot, but in good accordance with the theoretical value. Haber and LeRossignol's results for the equilibrium at atmospheric pressure do not agree with those of Nernst and Jost, as Q was found to be 24,000 cals. Nernst maintained that the output at atmospheric pressure was too small and inaccurate to base any conclusions upon it. Nernst's results are of technical interest in so far as they show that the ammonia output at high temperatures is only one-third of what has been expected on the bases of Haber's figures.

F. Jost who worked with Nernst, carried out experiments using a furnace as above described, and temperatures of 685° to 1040° . An equilibrium was reached from both sides, first by passing a mixture of one part of nitrogen and three parts of hydrogen at a pressure of 50 atmospheres, through the furnace and determining the amount of ammonia formed, and secondly, by passing a similar mixture

containing 20% ammonia and determining the amount of ammonia present. The results of a series of measurements agree satisfactorily and can be expressed by the formula:

$$\log X = 3065T - 6.918$$

where X is the partial pressure of ammonia formed from a mixture of three parts of hydrogen and one of nitrogen at a pressure of one atmosphere. Thus at 1000° , X was found to be .0032% while the above formula gives $X = .00308\%$. By means of Van Hoff's isochore the heat of reaction was calculated to be 28000 cal. as against a value of 24000 cal. as found by Thomsen and Berthelot.

Nernst points out that known volumes of two gases were passed successively at the same rate through a copper tube containing silver shavings and then through a small silver calorimeter placed completely inside an electric furnace. The copper tube projected some distance into the furnace owing to radiation, etc. Its temperature was measured very accurately and was found to be 200° lower than that of the calorimeter when stationary conditions had been reached. The comparative amount of cooling produced in the calorimeter by the passage of the various gases was measured by means of a differential thermo-element, the second junction of which was situated in the internal copper lining of the furnace. The heat change corresponding to the reaction $3H_2 + N_2 = 2NH_3$ at 850° is 30200 cal. with an uncertainty of 1500 cal. This is close to the value 28000 cal. calculated from the measurements of Jost, but is far from 25000 cal. calculated by Haber and LeRossignol.

From the above we see the ammonia equilibrium is far from settled. Now turning aside from the physical aspect of the subject, let us look into some of the processes devised by numerous inventors. We may, as L. Mond suggests, divide the processes of this kind into three classes:

1. Processes which aim at the combination of hydrogen and nitrogen at high temperatures; or with the assistance of electricity, or in the presence of acid gases.
2. Processes in which primary nitrides are formed, which are afterwards transformed into ammonia.
3. Processes in which primary cyanides are formed.

With this division in view it is the writer's intention to describe one or two of the more promising processes in each division, with a special stress on sub-division 1.

Several inventors aim at utilizing the intervention of the boron nitride for forming ammonia. Thus N. Basset heats coal impregnated with boric acid, and covered with a layer of magnesia, lime, oxide of manganese, etc., in a retort, and passes nitrogen over the mixture. When a sufficient quantity of boron nitride has been formed, steam is introduced, and the ammonia now obtained is carried away.

G. N. Tucker mixes carbon, impregnated with borates, with alkaline carbonates, or the oxides of manganese, antimony, iron, titaniferous iron, or with the borates of these metals. These are

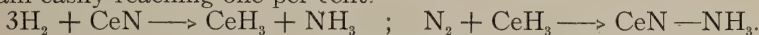
exposed to a red-heat in retorts; gas rich in nitrogen is passed in, so that the nitrogen combines with boron; then steam is passed in, which is decomposed by the carbon or the metal, and supplies the hydrogen necessary to form ammonia, or else air or nitrogen and steam are mixed before introducing into the retort, in the proportion of 3 vols. steam to 1 vol. of nitrogen. The borates and the metallic oxides contained in the residue are to be used over again. The gas is purified, by milk of lime, from carbonic acid, hydrogen sulphide and tarry substances.

Mond believes that boron nitride cannot be utilized for the purpose in question, owing to the high temperature required for its formation and the volatility of boric acid with steam. More success seems likely to be obtainable by Lessie du Motay's plan of preparing titanium nitride, and allowing a mixture of nitrogen and hydrogen to act upon this. Titanium forms two nitrides, the higher of which is at high temperatures reduced to the lower by hydrogen, with the formation of ammonia. When passing a mixture of hydrogen and nitrogen over the higher titanium nitride, Mond never obtained so much ammonia as would be formed without any free nitrogen. Hence the lower nitride does not combine with more nitrogen, which makes the process impossible.

Kaiser obtains ammonia by heating calcium nitride in a current of hydrogen under high pressure; the calcium is reduced to the metallic state, or to the hydride when the hydrogen is in excess. If now nitrogen is passed over it calcium nitride is reformed. A continuous production of ammonia can be effected by heating metallic calcium alternately in a current of nitrogen and hydrogen. This takes place all the more readily when the metal is deposited on asbestos in a finely divided state. The reaction sets in at about 150°C; the best results are obtained between 200° and 400°C.

Borchers and Beck prepare nitrides of metals from atmospheric nitrogen by the assistance of the electric current in a similar way, as in the electrolysis of alkaline chlorides, where the cathodic mercury is charged with alkaline metal, which is taken out of it, so that the mercury can be used over again. An alloy of tin and magnesium electrolytically formed, is by the action of nitrogen in another space partially converted into magnesium nitride; the alloy now containing much less Mg, returns to the cathode space to be again enriched with Mg. The magnesium nitride is converted into ammonia by means of water or of steam, and the process may be conducted in such manner that anhydrous ammonia and anhydrous MgO are formed. The latter is used over again in the electrolytic cell.

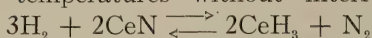
J. Lipski¹ says that in his process of using cerium nitride the yield of ammonia is considerably greater than has hitherto been obtained by similar processes, the volume of ammonia in the gas stream easily reaching one per cent.



The above takes place at atmospheric pressure and at low

1. Z. Electrochem, 1909, or J. Soc. Chem. Ind. 1909.

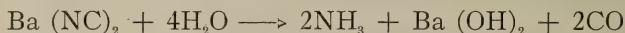
medium temperatures without interference from the reaction,



although at high temperatures, when the dissociation pressures of the nitride and hydride are greater and the stability of ammonia is small, the last reaction predominates; the temperature most favorable to the formation of ammonia by this process is $200^\circ - 300^\circ\text{C}$. The gases must be pure and dry, traces of moisture affecting the surface of the material and rendering it useless. By employing nitrogen and hydrogen alternately a continuous production of ammonia takes place.

Having executed the work of ammonia synthesis from the nitrides of metals, let us discuss the formation of it from the cyanides or carbides. As was the case in the nitrides, much work has also been done on this branch of the subject and many inventors have patented their discoveries.

In 1860 Margueritte and Sourdeval found that caustic baryta is very active towards nitrogen, because it is neither fusible nor volatile. The former quality prevents the external fusion of the mass, whereby the action of the gases on the interior is impeded; the latter prevents loss by volatilization.



They made a mixture of native barium carbonate with coal tar, pitch and sawdust, with or without iron filings, which was strongly ignited in a fire-clay retort till the barium carbonate had been converted into a porous mass of barium oxide. Through this they passed at the proper temperature a slow current of air, the oxygen of which had been previously converted into carbon monoxide by red-hot coal, thus barium cyanide was formed. This was cooled down to 300° and steam was passed through. All the nitrogen of the cyanide is evolved as ammonia, and the barium hydrate remaining behind may be used over again. This process did not pay owing to technical difficulties.

Margueritte and Sourdeval's process was taken up again by L. Mond who carried it out in the following form. The barium carbonate is powdered and incorporated with small coke from pitch or oil residues, charcoal, pitch, tar, paraffin residues, and so forth. In lieu of barium carbonate it is possible to employ a solution of its oxide or salts, or of alkaline oxides or salts; for instance the solution obtained by lixiviating the used briquettes. The most advantageous proportions are; Thirty-two parts barium carbonate, eight parts of charcoal or coke, and eleven parts pitch. The addition of alkalis is not of much use. This mixture is formed into briquettes, which it is necessary to heat in the reducing flame till the pitch is coked, and the barium carbonate converted partially or completely into oxide. The briquettes may be broken up into small lumps, and such lumps may also be formed by heating the mixture of barium carbonate or carbon on the hearth of a reverberatory furnace or in a revolving furnace by means of a reducing flame until the mass is fritted, when it is discharged and broken up into lumps.

These lumps or briquettes are charged into kilns arranged in the same way as an annular kiln, so that some of the chambers are being heated while others are cooling down, or are being filled or emptied. A gaseous mixture, as rich as possible in nitrogen, and containing little carbonic acid, oxygen and aqueous vapor, heated to a temperature of about 1400°C ., is passed into the chambers filled with briquettes, until a sufficient quantity of cyanogen compounds has been formed. When this is the case, the stream of heated gas is shut off, and cold gas of the same or similar composition conducted into the mass until the temperature has fallen to 500°C . The stream of gas is now suspended and the material treated with steam; the ammonia hereby resulting, is aspirated off and absorbed or condensed. As sources of nitrogen, the gases evolved from the carbonic acid absorption apparatus of the ammonia soda process, and the gaseous mixture obtained by the combustion of coal or coke with the smallest possible quantity of hot air, are the most profitable; and the requisite temperature is most readily obtained by means of a Siemens recuperator applying this also to the previous heating of the air employed for the combustion. The gases leaving the last chamber, which is being heated at the time must be further cooled down by passing them under a boiler or pan, or through a washing apparatus, before they get into the chamber where the material is just cooling. After having fulfilled this object, these gases, which contain much carbon monoxide, may be burned and used as a source of heat, for instance, for heating air, generating steam, and for other purposes.

This process, although tried on a somewhat large scale, did not come into practical operation. The process requires a very large amount of heat to be communicated through the earthenware sides of a retort, which wastes too much fuel, even if retorts similar to those of zinc works are employed. This cannot pay whilst so many other sources of ammonia are available.

Herman Mehner¹ has however, devised a long and drawn out unique process for the production of ammonia from cyanides. His invention has for its object the improvement of the process of manufacturing nitrogen compounds from atmospheric nitrogen, producer gas or other suitable gaseous mixtures by having them react with carbon in the presence of alkaline matter, such as hydrates and carbonates of alkaline and alkaline-earth metals, also to do away with loss of heat due to radiation, etc. He causes the mixture of carbon and an igneous fluid heat-carrier, such as molten salts, as silicates, preferably alkaline silicates, scoria, slag, cinder and other suitable compounds or salts, and also molten metals, as iron and the like, to percolate through in the presence of alkali. Air or other suitable gases containing nitrogen are allowed to penetrate through at an intermediate zone in the furnace. The current of air is subdivided in the furnace into a strong upward and a weak downward current. By this the furnace is divided into an oxidizing zone, a reducing zone and a reacting zone. The oxidizing zone is the upper one, where owing to the larger supply of oxygen the combustion will substantially result

1. U. S. Pat. No. 754474 of 1904.

in carbonic acid, and consequently a correspondingly large amount of heat is produced, which is taken up by the percolating heat carrier, the carbonic acid escaping through an opening. The reducing zone is the one below the oxidizing zone, where as a consequence of the smaller supply of oxygen, the carbon is burned only to carbon monoxide. The heat generated is added to that of the heat carrier, and both supply the zone below with the necessary heat for the reaction, and moreover, the lowest zone is held free of any carbonic acid gas thus preventing the cyanide reaction from being disturbed. The slag returns to the top of the furnace and repeats the percolation.

The furnace resembles a shaft furnace provided at the top with a hopper for supplying carbon and a vessel for supplying the molten slag. A lid, which is sealed by a sand seal, closes in the hopper. The furnace is filled with coke, divided into suitable pieces. About the middle of one side of the furnace is the tuyere for admitting the hot air and an arrangement to divide it into two currents as above described. The molten slag then percolates through and is removed at the bottom to repeat the operation. In this process incandescent coke, nitrogen and sodium vapors, obtained from the slag, are brought into intimate contact with each other in the presence of such catalysts as iron, etc. Thus, sodium or alkaline cyanides are formed which are converted into ammonia by means of steam.

The Method of the Synthesist.

Let us now say a few words in regard to the synthesising of ammonia from its elements, namely nitrogen and hydrogen. This is accomplished in several ways, such as the use of a catalyst, the silent electric discharge and so on.

E. P. Perman states that ammonia cannot be synthesised from nitrogen and hydrogen by the action of heat alone; the decomposition of ammonia by heat at 800–1000°C. is therefore irreversible. Synthesis may be accomplished (in small quantities) when the gases are partially ionised, as by sparking them, or by exploding them with oxygen, or by heating them with many of the metals in the presence of moisture.

Many inventors have worked upon this principle, some succeeded in getting fair results while others were not so good. Upon diagnosis of this case I have decided to describe a few of the processes now in use.

Haber and Le Rossignol have now discovered that on passing gases containing nitrogen and hydrogen over osmium large quantities of ammonia can be obtained.

In order that this process should be successful, it is advisable that the combination take place at as low a temperature and as quickly as possible, since when the temperature increases the concentration of the ammonia formed decreases.

In carrying out this invention, osmium can be used either in the form of the metal, in a very finely divided condition, or in the form of a compound of the metal, which on being used becomes converted into metallic osmium, such as, for instance, osmium oxide hydrate,

(prepared by the reaction of formaldehyde on an alcoholic solution of osmic acid), or as Fremy's salt.

The osmium is precipitated on a suitable carrier such as quartz, asbestos, clay and so on.

At 200 atmospheres pressure, and in the presence of suitable contact substances, nitrogen and hydrogen combine to form ammonia in sufficient quantity for practical exploitation of the process. The reaction is very incomplete, and it is necessary to remove the ammonia as it is formed, which can be achieved by a system of circulation of the gases at high pressure. The ammonia is condensed and can be removed either as a gas, or as anhydrous liquid; the uncombined gases continue to circulate throughout the high pressure system. In a small experimental apparatus, built at the Karlsruhe Institute for Physical Chemistry, 90 grams of liquid ammonia were produced per hour at 185 atmos. pressure. Osmium is the most active contact material for this purpose, at 175 atmos. pressure and temperature of 550°C. yields of 8 volumes per cent of ammonia can easily be obtained from the mixed gases of 1 vol. of nitrogen and 3 vols. of hydrogen.

As the amount of available osmium is very small, another more easily obtainable catalyst was sought for and was found in the form of uranium containing a certain amount of carbide, or carbon, as obtained by the reduction of the oxide with carbon in the electric arc. In the gaseous mixture at high pressure this is transformed into a very fine powder, with the absorption of nitrogen, and this power exerts a powerful catalytic action of the gaseous mixture at a temp. below 500°C. The power necessary for compression and circulation of the reacting gases is very small. The efficiency of the heat exchange appears to be of subordinate economical importance, and the industrial exploitation of the process may soon be looked for.

L. Brunel and P. Woog,¹ after unsuccessful efforts in the formation of ammonia by passing a mixture of pure hydrogen (3 vols.) and nitrogen (1 vol.) over thorium and cerium oxides, palladinised pumice, quicklime, soda lime, calcium chloride, calcium molybdate, anhydrous barium or strontium oxide, manganese dioxide, aluminium phosphate or magnesium phosphate, at 15° to 350°. However, green nickel oxide hydrated spread thinly over fragments of powdered glass, is heated in a current of dry air and a mixture of hydrogen and nitrogen is then passed over the sesquioxide thus formed, heated to 180°–200°C. A small amount of ammonia and water is formed, on the passing a mixture of air and excess of hydrogen, the nickel oxide is alternately reduced and reoxidised with evolution of much heat, and a continuous formation of ammonia and water results so long as the temperature is kept below the incandescence of the oxide. The requisite cooling is effected by suspending the nickel oxide in a liquid which boils at the temperature at which ammonia is formed and thus absorbs the excess of heat. Petroleum B.P. 200°–240°C. is found to answer this purpose and by its intervention a regular formation of ammonia is obtained.

1. J. Soc. Chem. Ind., 1907.

H. C. Wolterreck states that ammonia is always formed when a mixture of pure hydrogen and nitrogen is passed over reduced iron heated to a dark red heat. This formation, however, soon ceases, and a careful study of the conditions has demonstrated that the formation was due to the presence of oxygen in the form of iron oxide, since iron freshly reduced by hydrogen and not exposed to the air will not produce a trace of it. Careful experiments have shown that the presence of oxygen is essential to the formation of ammonia, and that the contact material employed must be able to act as a carrier of oxygen.

When a mixture of 3 vols. of hydrogen and 1 vol. of nitrogen is passed over reduced iron, spread in thin layers on asbestos fibre, and heated to 550°C. small quantities of ammonia are formed. The yield is increased by the oxide of the metal, but in both cases the yield stops after a time. Similar results are obtained with the oxides of nickel, cobalt, cadmium, silver, lead, bismuth, chromium, the last two giving the best yields. The reaction is made continuous by replacing the nitrogen by air, and the results are improved by the introduction of water vapor, whilst the hydrogen can be replaced by coal gas freed from nitrogenous products. The passage of 100 liters of a mixture of hydrogen (one vol.) and air (78 vols.) through water kept at 80°C. and then over iron oxidised and reduced by carbon monoxide, before the experiment, gave at different temperatures the following amounts of ammonia:

260 - 800°C.	.0803 gm.	400 - 450°C.	.0134 gm.
300 - 350°C.	.204 gm.	450 - 550°C.	.0411 gm.
350 - 400°C.	.119 gm.	550 - 650°C.	.0236 gm.

All the experiments occupied 4.5 hours. The results show that 300-350°C. is the most favorable temperature. Diminishing the velocity of the gas, i.e., prolonging its contact with the iron, diminishes the yield. Other oxidisable materials which can be substituted for the reduced iron are coke and wood charcoal, but better results are obtained from peat. A series of comparative experiments using sugar charcoal, and varying the temperature, the volume, and the velocity of the mixed gases, show that the best results are obtained at 450°C. with 40 l. of gas passing 6 hours when .9 gm. of ammonia was formed per 100 gms. of charcoal burned.

E. Briner and E. Mettler form ammonia from its elements by the action of the electric spark, at the temperature of liquid air. A mixture of 3 vols. of hydrogen and one vol. of nitrogen was introduced into a flask fitted with platinum electrodes and a spark passed across the electrodes. In order to avoid the decomposition of the ammonia formed, they cooled the flask with liquid air, thus liquifying the NH_3 formed. With this device it was found that the yield of ammonia increases with the intensity of the primary current up to a certain point and then decreases. For example, with a current intensity of 1.7 amps. the yield of NH_3 was 25 mgrs. per kw. hr., while with 2 and 2.6 amps. respectively the corresponding

values were 55 and 42 mgrs. They state that the silent electric discharge gives better results than the spark discharge at the temperatures of liquid air. Other experimenters add a little of some acid to their mixture of N_2 and $3H_2$ to remove the ammonia as it is formed, in order to do away with the cooling of the flask. The authors state that working with a pressure of 100 mm. of mercury they obtained their best results.

Nithack has a very nice apparatus for the production of ammonia. He saturates water under high pressure with gaseous nitrogen and then passes electricity through the water. He states that the nitrogen is quantitatively transformed into ammonia.

Although these processes above described are very interesting, yet while the ammonia from the gas works is obtained in such copious quantities, these methods are not yet working on a commercial scale, and we must wait until some easier and cheaper method is devised until we are able to compete with the ammonia, which is obtained as a by-product from the gas works.

In the describing of the above processes, the writer has only dealt with those experiments which give hope of practical exploitation of this subject.

In the Laboratories of the University.

Let us now turn to the writer's experiments upon this problem. An attempt has been made to synthesise ammonia from its elements in several ways, namely, by the use of a catalyst, the bringing together of nitrogen and nascent hydrogen, and by the reduction of nitric acid.

Figure 1 will show the apparatus used by the author for the bringing together of nascent hydrogen and nitrogen. It consists of a glass spiral, through which a platinum wire runs. The platinum wire is supported on glass beads at close intervals, this was to enable the wire to be forced around the spiral, and at the same time to keep it away from the walls of the tube. This wire was made the cathode of the cell, while the anode was a lead strip. The electrolyte was dilute sulphuric acid.

By means of a delivery tube nitrogen from a gas holder was made to bubble around this spiral and when the current of 220 volts and $\frac{1}{2}$ amp. was run through this, electrolysis commenced. By this method the nitrogen came in contact with the nascent hydrogen liberated from the wire.

This experiment proved fruitless, as hydrogen was not liberated from the whole of the wire, but just from about $\frac{1}{2}$ inch of the wire

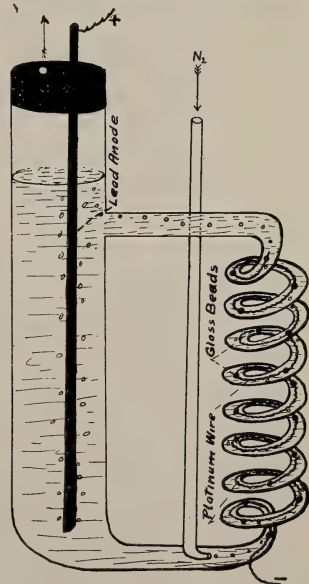


Fig. 1
Apparatus for Combining Nascent
Hydrogen with Nitrogen.

which was nearest the other electrode. In this manner the nitrogen did not have a fair chance for its combination.

A lead spiral was substituted for the glass one, and the whole spiral was made cathode, while the anode was lead, the electrolyte as before being dilute sulphuric acid. Nitrogen was introduced in a similar manner as above described. Here also the experiment gave no evidences of any ammonia having been formed, when tested with Nessler's solution.

During the electrolysis the whole apparatus was immersed in a pail of cold water to prevent the apparatus from becoming too hot and thus cracking.

In all these experiments the nitrogen used was made by making a saturated solution of 1 part of sodium nitrite and $1\frac{1}{2}$ parts of ammonium sulphate and by mixing these in a flask, to which a little potassium bichromate has been added in order to oxidise nitrous fumes, a nice gentle stream of gas can be obtained which should be washed, through dilute sulphuric acid to remove nitrous fumes, before being used.

Another scheme attempted by the author for bringing nitrogen in contact with nascent hydrogen, was the use of a porous graphite tube, which was to act as cathode of a cell, while nitrogen was forced through the tube, and allowed to diffuse through the pores, and thus come in contact with the hydrogen liberated from the acidulated water, which was to act as electrolyte. This attempt failed, in so much as the porous graphite tube could not be made.

Much time was spent in an attempt to produce a suitable porous graphite electrode. Anthracite, coke and bituminous coal were ground to about 20 mesh, and ordinary salt was also pulverized very finely. A mixture of about 80% coal and 20% salt was stirred up to an adhesive mass by the use of various sticky substances such as molasses, engine oil, vaseline, mucilage and glue. This mass was then rammed into a mailing tube, down the centre of which ran a glass tube surrounded by a paper oiled with vaseline. After the tube was filled, the glass tube was easily withdrawn from the mailing tube, on account of the viscosity of its surface, thus leaving a space in the centre of the mailing tube surrounded by the carbon.

The mailing tube was allowed to stand at room temperature for two or three days, then finally dried in the steam oven. After the drying was completed the tube was baked in a muffle, the temperature of which was raised very slowly, for about four hours. The muffle was allowed to cool slowly and the tube removed and placed in a high resistance furnace.

The high resistance furnace was built of magnesia fire brick. The carbon electrodes were buried in crushed coke and the tube placed in the centre of this coke between the electrodes, the whole being covered with coke and finally with bricks. A current of 200 amperes was allowed to pass through this mass for about $2\frac{1}{2}$ hours or until a very bright red heat had been attained, after which the current was shut off and the furnace allowed to cool.

Eight attempts to produce this tube were unsuccessful, after

using various coals and adhesives, as the tubes after placing in the electric furnace no longer held their rigidity, but would fall to pieces as soon as they were touched.

The salt was to be leached out of the tube and thus leave it porous. For future references the writer would call the reader's attention to a paper published in "The Journal of Industrial and Engineering Chemistry," Vol. 1 of 1909, pp. 286, on the "Manufacturing of Carbon Electrodes." This paper treats with the manufacturing of electrodes on a commercial scale, which could not be attempted in the laboratory.

In order to get around this difficulty a lead tube was substituted for the graphite tube. The tube was drilled with several very fine holes, thus making it porous, so to speak. Nitrogen was allowed to diffuse through these holes and thus mingle with the hydrogen liberated.

This experiment also proved fruitless, as the nitrogen could not be kept from spurting out of these holes away from the hydrogen altogether. If the pressure upon it were decreased then a spasmodic spurting would result and no contact could be effected.

The lead tube was finally discarded and the reduction of nitric acid attempted. Figure 2 shows the apparatus used. A quenched copper cathode in the shape of a spiral, and a platinum anode were used. The anode was made by sealing a piece of platinum wire at both ends into a glass tube and then filling the tube with mercury, thus doing away with a great excess of platinum wire.

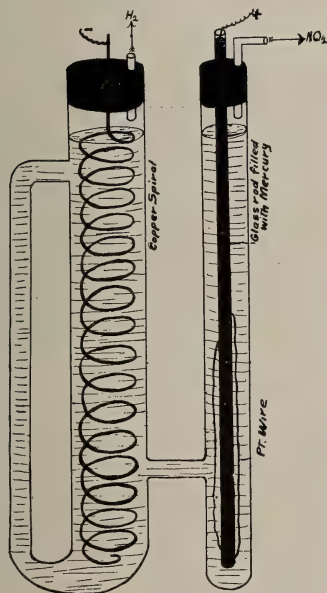


Fig. 2

Electrolytic Reduction of Nitric Acid.

The electrolyte consisted of nitric acid and sulphuric acid in various strengths and proportions.

The experiments were carried out under variable conditions, produced by varying the temperature of the electrolyte and changing the current density. In order to alter the temperature of the electrolyte the apparatus was immersed in water kept at the temperature required.

Julius Tafel¹ points out that when nitric acid is electrolysed, it suffers reduction, and in order to diminish the action of the nitric acid as an electrolyte a relatively large amount of sulphuric or hydrochloric acid was added to the solution. The product of the reduction is largely dependent on the nature of the metals used as electrodes. With platinum no appreciable reduction takes place and with palladium the reduction is extremely slow. The chief

1. Zeit. Anorg. Chem. 31. p. 289-325.

products of the reaction are hydroxylamine and ammonia. The largest proportion for hydroxylamine is formed when mercury is used as the electrodes. With lead electrodes about 40% of the nitric acid is converted into hydroxylamine, and with copper electrodes only about 15%. If the copper be spongy, caused by quenching, only about 1% of the acid is converted to hydroxylamine, the remainder being reduced to ammonia. When an amalgamated electrode is used, the reduction takes place in the same way as when a mercury electrode is employed.

Hydroxylamine is not altered when subjected to electrolysis between copper electrodes. It is thus proved that the reduction of the nitric acid takes place in two ways independent of each other, the one giving hydroxylamine, the other ammonia; the course of the reaction depends on the specific nature of the electrodes.

The following table gives Tafel's results upon this subject.

2.4 amp. and temp. 0°C.

Cathode material	Surface	Time in hours	NH ₂ OH	NH ₃	HNO ₂	gas	sum
Pb.	prepared	2½	26.8	57.6	1.5	7.0	91.4
"	"	2½	25.2	57.6	0.6	8.4	91.2
"	"	2½	22.2	64.6	.3	6.5	93.3
"	amalgam.	2½	69.7	16.9	.1	9.2	95.8
Sn.	blank	3	45.8	38.3	.8	7.7	91.8
"	"	3	40.8	42.5	.6	6.9	90.2
Cu.	"	2½	11.5	76.8	trace	7.1	95.4
"	spongy	2½	1.5	93.8	"	"	"
"	"	2½	1.0	92.3	"	3.4	96.7
Ag.	blank	3	18.4	47.2	1.5	21.	86.6
"	"	3	25.3	"	"	18.5	"

In using .4 gm. HNO₃ 20 cc. 50% H₂SO₄, 10 sq. dcm. kathode surface.

In the writer's experiments along this line, the current was allowed to pass for approximately 5 hours after which the solution in the cathode compartment was removed and made alkaline by the addition of caustic soda, and then distilled, the issuing gases passed through standard acid. By titration the amount of ammonia formed was determined.

The following table gives the results obtained by the author.

%N H ₂ SO ₄	Gms. 100% ¹ HNO ₃ used per 200 cc. H ₂ O	current	time	temp.	gms. NH ₃	%
20	3.57	.5 amp.	5 hr.	20°	.415	43.1
20	1.76	.5 "	5 "	20°	.465	97.7
20	3.57	.5 "	5 "	0°	.458	47.5
20	1.76	.5 "	5 "	0°	.460	96.6
30	3.0	.5 "	5 "	0°	.498	87.9

From the results obtained here, the time required to reduce one pound of 70% nitric acid is 905 hours, or 99.5 kilo-watts will be used in the reduction at a cost of 3 cents per k.w.hr. which amounts to \$2.98.

¹ This 200 cc. of acid was the volume of the cathode solution, being composed of N.H₂SO₄ and ½ or ¼ N.HNO₃.

As there is not much use for hydrogen at the present time, this by-product will be of little use in defraying the cost of reduction.

From the 318.5 grms. of pure 100% nitric acid or 454.5 grms. of 70% acid, one should get 84 grms. of ammonia, going on the assumption that 97.7% of the acid was reduced.

Of course, this product is not obtained as fort ammonia, but probably the majority of it will be neutralized by the sulphuric acid which is present, thus forming ammonium sulphate and also ammonium nitrate. Therefore, to recover the ammonia from these salts they must be treated with lime at a further expense.

As there are other cheaper methods of producing ammonium sulphate the author believes that this process is too expensive for technical working, as in the first case if a stronger acid than $\frac{1}{2}N$ or $\frac{1}{4}N$ is used, the copper cathodes are going to be attacked, and this weak acid necessitates a larger plant, more cells, more men, etc., and in general, more expense, than if the concentrated acid could be reduced.

Figure 3 shows the general layout of the apparatus used in the attempt to synthesise ammonia by catalysis. It consists of an nitrogen holder, an electrolytic hydrogen producer and an electric furnace.

The nitrogen which was obtained from ammonium sulphate and sodium nitrate as previously described was held in a gas holder and allowed to slowly bubble through a concentrated potash solution to

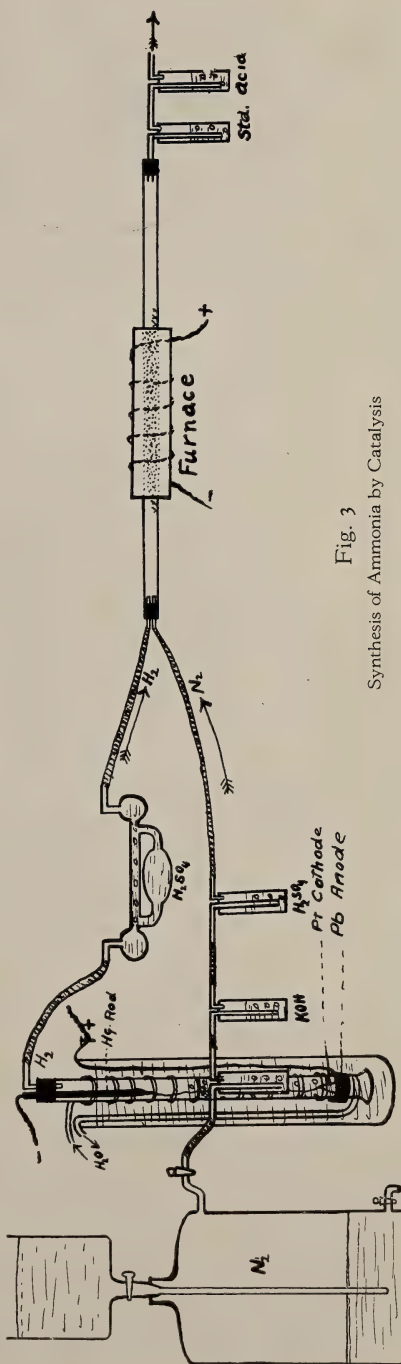


Fig. 3
Synthesis of Ammonia by Catalysis

remove nitrous fumes and any carbon dioxide, then through conc. sulphuric acid to completely dry it, before it was allowed to enter the tube containing the catalyser.

The hydrogen was obtained from the electrolysis of acidulated water. Figure 4 shows a diagram of this apparatus. It consists of a large glass cylinder which holds the acid, and a tube open at both ends suspended in the centre of this cylinder so that the bottom end of it is about one inch away from the bottom of the cylinder. A two-holed tightly fitting cork is placed in the upper end of this tube, through which run two glass tubes, one is for the exit of the hydrogen gas and the other tube dips about six inches into the acid in the tube. A platinum wire is sealed in the end of this tube and runs down to connect with the platinum cathode situated in the tube nearly at the bottom. The glass rod is then filled with mercury and thus contact results. The glass rod serves the purpose of keeping the platinum

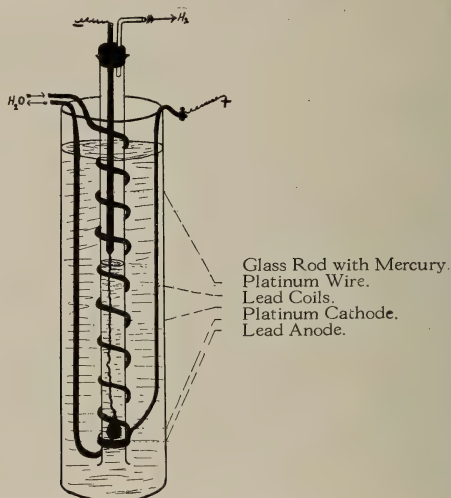


Fig. 4. Electrolytic Hydrogen Generator.

wire away from the sides of the tube and thus preventing the tube cracking if the wire should get hot due to too much current passing through it.

The anode consists of a lead strip dipping almost to the bottom of the cylinder, but so arranged as not to allow any oxygen to find its way into the central tube, and thus mingle with the hydrogen. The electrolyte was kept cool, by means of a lead coil placed in it, through which water was allowed to circulate.

The hydrogen was washed in a specially constructed wash-bottle containing concentrated sulphuric acid, by which means it was dried. This wash bottle, as may be seen in Fig. 1, overcomes the friction caused by the head of liquid in an ordinary wash-bottle, and thus delivers a continuous stream of hydrogen instead of a spasmodic one, as would be obtained by the use of an ordinary wash-bottle.

After the gases have been thoroughly dried, they enter the tube containing the catalyser supported on asbestos, in the proportion of approximately 1 vol. of nitrogen to 3 of hydrogen. The tube was heated by passing it through an electric furnace, the temperature of which was regulated by means of a rheostat.

The issuing gases were bubbled through standard acid, and any ammonia formed was determined by titration.

Experiments were carried on using different temperatures and catalysers, also by using dry and moist gases. The gases were made moist by allowing them to bubble through warm water instead of conc. sulphuric acid.

The following are the results which were obtained during a period of six hours.

Catalyst	temp.	gas.	gms. NH ₃
Thorium oxide	500	dry	0
"	525	"	0
"	560	"	0
"	590	"	0
Uranium oxide	500	"	0
"	525	"	0
"	560	"	0
"	590	"	0
Tungsten oxide	500	"	0
"	525	"	0
"	560	"	0
"	590	"	0
Titanium dioxide	290	moist	0
"	375	"	0.272
"	500	"	0.391
"	500	dry	0.799
"	525	"	0.612
"	550	"	0.442

All the above experiments were carried on at the pressure of the atmosphere, and the uncombined gases escaping from the standard acid were not caught and sent back through the tube again, so the efficiency of the method was not calculated. However, I believe that if a pressure of some 150-200 atmos. were applied and that the experiments were carried on in a circulating apparatus somewhat similar to that of Haber's, that titanium dioxide would serve as an efficient a catalyst as osmium which he used.

The synthetic production of ammonia was also attempted by the production of chromium nitride. Chromium oxide was made from chromic sulphate, and the metallic chromium produced by a thermite reaction. The metallic chromium was then placed in a combustion tube and heated to red heat while a current of nitrogen was lead into this tube. No reaction between the metal and the gas could be effected however, as the tube would not stand the temperature.

It was the author's intention to produce chromium nitride, and then by an alternate stream of hydrogen and nitrogen, which was to be lead over it at a certain temperature, to obtain chromium hydride and then reform the nitride, thus giving a practically continuous stream of ammonia. This process seems to work very well with other nitrides.

Another scheme suggested itself, and that is to surround the cathode of an electrolytic cell with the chromium nitride, which is not attacked by dilute sulphuric acid, and any ammonia formed would be neutralized by the acid, thus producing ammonium sulphate which would be sold for fertilizer.

The production of ammonia by this process is only theoretical as whether chromium hydride or metallic chromium would be produced when the nitride was used up, the author does not know.

If this process worked it would have advantages over the other nitride method in so much as it would make the manufacturer independent, because a person cannot buy hydrogen without curiosity being aroused, whereas one may buy electricity without questions being asked.

In concluding, I may say that I do not think it will be very long before ammonia is synthesised on a commercial scale, as both nitrogen and hydrogen may be procured very cheaply. One cubic meter of hydrogen compressed to 150 atmos. may be purchased in Germany for about three cents, while the nitrogen may be obtained from the atmosphere.

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H. V. Armstrong, '09, is superintending a water-works installation at Estevan, Sask., for Chipman & Power.

W. G. Collinson, '09, is at Durham, Ontario, as analytical chemist for the National Portland Cement Company.

Messrs. W. G. Worden, '11, B. H. Hughes, '14, M. G. Cameron, '09, and O. W. N. Charlton are recent additions to the Hydrographic Survey Department of the Interior. Their work lies in the vicinity of Lake of the Woods and west to the Red River.

L. S. Cockburn, '10, and E. L. Wenger, B.Sc., have become partners under the firm name of Wenger & Cockburn, consulting engineers, with headquarters in Regina.

W. M. MacAndrew, '11, is sales engineer with Allis-Chalmers-Bullock, Limited, in the Vancouver office.

SOME NOTES ON THE OAKVILLE VIADUCT AND THE DYNAMITING OF THE CONDEMNED ARCH RIBS, AUGUST 12th, 1912¹

By C. H. CUNNINGHAM, B.A.Sc.

On Tuesday, August 13th, a rather interesting, and certainly unusual, event took place in Oakville when the big arch ribs forming the main span of the concrete viaduct under course of erection there, were dynamited. The arch span consisted of two ribs side by side, with vertical concrete posts carrying the slab and girders of the floor system.

These ribs had been completely concreted, but owing to several very serious faults in the construction, it was deemed advisable to destroy them and rebuild.

It was during the summer of 1911 that the county of Halton decided to call for tenders on a reinforced concrete viaduct over the 16-mile creek on the middle road between Oakville and the township of Trafalgar. Competitive designs in steel and reinforced concrete had already been prepared, calling for a clear roadway of eighteen feet. It was decided to adopt the concrete design and reduce the clear roadway to sixteen feet. Accordingly, these plans were prepared by Frank Barber, C.E., Toronto, as consulting engineer for Halton county, and on August 23rd, the contract was awarded. Two schemes were submitted, one of which called for the floor to be 40 feet above ordinary water level, and the other at 50 feet. Owing to the better grades obtainable on the approaches the latter plan was the one adopted.

The main features of the design are, a cantilevered slab floor supported on two main girders of various spans of 9 feet centres, which frame into square posts supported on heavy concrete piers, the stream itself to be spanned by a double rib arch of 135 feet 6 inches clear span on which the floor is carried by vertical posts and small girders. The arch ribs are of uniform width throughout, being 3 feet 3 inches square at the crown and increase in depth to 5 feet 6 inches at the skewbacks. The floor slab has an average thickness of 12 inches, and is reinforced entirely with $\frac{3}{4}$ inch round rods, cantilevering about four feet on each side.

The girder spans, which form the viaduct approaches on each side of the arch are eight in number, six being on the west side; and range in lengths from 34 feet to 48 feet.

The parapets are also of concrete, and have practically no ornamentation. In fact, the whole structure is noticeably plain. Immediately that the contract was awarded work was begun, in order to get as much done as possible before frost set in. Concreting actually commenced on the footings on October 5th, and by the end

¹ In view of the recent controversy on the relative merits of steel and concrete, it would be well to remind the reader that faulty construction and insufficient safe-guarding of the concrete in freezing weather, were the factors which determined the engineers in condemning this work. The arches are being rebuilt on the original design which is considered in every way to be adequate. This article is not intended in any way to throw aspersions on concrete or concrete design. It simply aims to describe the method employed in blowing out the condemned ribs. It appeared elsewhere in a recent number of the *Canadian Engineer*.

of November the arches were ready to concrete. It was at this point that the regrettable trouble ensued which culminated in the contractor going ahead contrary to the engineer's orders and concreting the arch ribs on centering which was not sufficiently braced. An injunction and law suit followed, but meanwhile the arch ribs had been finished.

An investigation followed and showed up a considerable number of defects in the arches as erected. Also the weight of concrete was found to have been too great for the centring, which had shifted and thrown the centre line of the ribs out of a vertical plane to the extent of about three inches at places. Probably no one of the faults in itself would have been sufficient to condemn the arches, but when

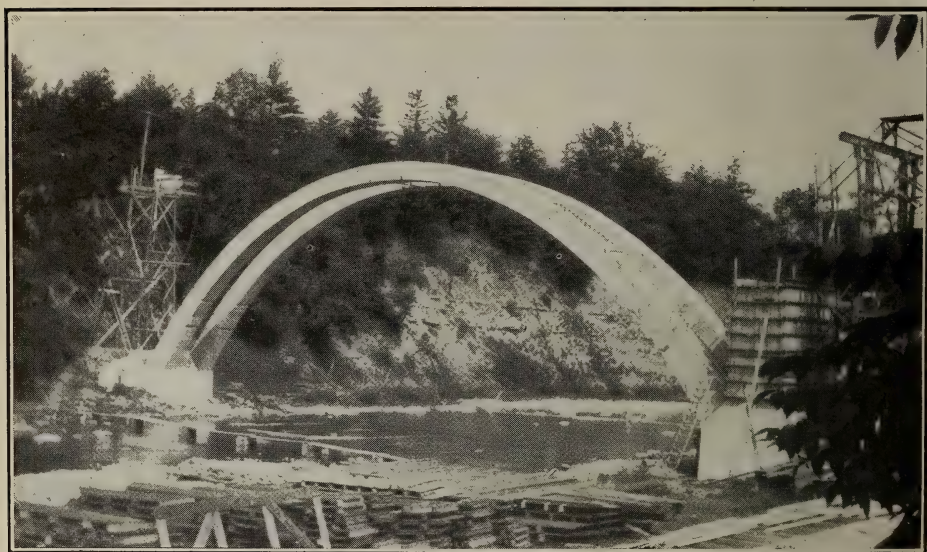


Fig. 1—Showing the Arch just before the blasts. (The notches where the rod were cut are plainly visible.)

all were summed up, the engineers did not feel that they could stand behind the structure as it was then, and recommended rebuilding then.

An adjustment was finally arranged and the original contract cancelled. Work was not resumed till the spring, when another contractor undertook to complete the job for the county on a cost plus 10 per cent. basis. Work recommenced the end of June, since when good progress has been made.

The council finally decided to blow out the old arches, and accordingly all preparations were made. The concrete outside of the reinforcing, which consisted of 16 bars $\frac{3}{4}$ inch diameter along the intrados and extrados, was chipped away and the rods themselves cut at two places near each end haunch. There was but one connect-

ing strut between the two ribs, situated at the crown. This was also severed and the ribs were blown out separately.

Charges were placed in the crowns and near each haunch.



Fig. 2. The First Shot. Blowing the South Arch. (The charge in the last haunch did not explode, leaving a long end as seen in Fig. 3.)

Dynamite was used and fired by the electric spark to ensure simultaneous explosions, although any one charge would have sufficed to destroy the arch.

The south rib was dynamited first, after which the charges were



Fig. 3. The Arches blown out and lying in the stream. (Note the grillage of rods shown at the break.)

placed in the north rib. No mishap occurred whatever, and the skewbacks on the main piers were left unharmed. The photographs here reproduced will show the appearance of the arch before, during, and after the explosions. The reinforcing rods kept the concrete from breaking up to a considerable extent, and it will require a great deal of extra work to clear the stream bed in order to place the new centring.

The steel rods, wherever they were exposed by the splitting of the concrete, were noticeably clean and entirely free from rust. Although these rods were simple rounds having no corrugations or other means of creating a mechanical bond, evidences of a very considerable bond were very plain.

From a military standpoint it might be interesting to note the ease with which such a structure as this could be destroyed by dynamite if so desired. One heavy charge, favorably placed, would be sufficient to preclude the passage of a stream that was not in itself readily fordable. However, it should be remembered that it took over a week for two men to cut the rods, in order that there should be as little damage done as possible to the skewbacks and piers.

MATERIALS FOR ELECTRICAL INSULATION

By N. D. SEATON, B.A.Sc.

In the study of the subject of insulation, one is naturally led to ask, "Why does a thing insulate?" The answer might be given that it insulates because it is possessed of two distinct properties; first, the ability to stand the mechanical and electrical stresses due to the voltage used; and second, a conductivity such that but a negligibly small current can flow through it and break away. The first property is called the dielectric strength of the insulation, and the second, the ohmic resistance. The two together form its insulating power.

Electrical work is divided into two branches, wherein the requirements for insulation are widely different. In telephony and in telegraphy the voltages are low, so the dielectric strength is of relatively small importance: but the currents used are small, the circuits long, and an insulator of high ohmic resistance is required. On the other hand in apparatus designed for the generation and transmission of electrical energy, where the currents are large and voltages high, dielectric strength is the property mainly desired. This difference of requirements for an insulator gives to the term "insulation" a double meaning—to one branch meaning something having high ohmic resistance, and to the other, meaning something which has dielectric strength. The meanings are quite different since an insulator may have a high ohmic resistance and at the same time not resist high voltage breakdown. Air, which is about the poorest insulator in disruptive strength, has a very high ohmic resistance, while on the other hand insulating materials having the

best disruptive strength, such as mica, have a comparatively low ohmic resistance.

The above considerations, then, indicate the proper method of determining the fitness of insulation to withstand the conditions under which it must operate: that is, in testing samples we should actually subject them to electrostatic stress till they break down, and judge their quality by their dielectric strength and not by their ohmic resistance. The first cost of a machine for a given output depends largely on its rating, and that depends on the allowable temperature rise in the coils, and thus upon the temperature which the insulation of the coils will stand without deterioration. From this it follows that the quality of the insulation is of prime importance to users and manufacturers of electrical apparatus.

Conditions Influencing Tests on Insulation

In all insulation one of the greatest difficulties is to keep moisture from accumulating in it, it having an enormous deteriorating influence, and when a sample is to be tested, all the moisture should be removed. However, it does not do to dry samples of insulation too much, for this may lead to the sacrifice of their mechanical suppleness as well as a deterioration in their insulation resistance and dielectric strength. Moisture also has a depreciating effect upon the dielectric strength.

The insulation resistance decreases enormously as the temperature increases, not considering the effect of moisture. The influence of temperature on the dielectric strength is not nearly so much, and in fact, is scarcely appreciable as long as the material is not mechanically injured.

Every dielectric, whatever its thickness, requires a certain voltage to break it down, and this is proportional to the two-thirds power of its thickness.

In the case of insulation on a circular conductor, the volts per centimeter which the insulator will stand does not depend merely on the voltage and the thickness, but also on the curvature. A flat layer of insulator, say $\frac{1}{4}$ inch thick, will withstand a much greater voltage than the same thickness of layer bent around a small wire, and, therefore, having a greater curvature.

Ohmic Resistance Test

This test is usually made by placing the insulation across 550 volt direct current lines, in series with a moving coil voltmeter of known resistance. The machine tested must be set on insulating supports to prevent a short circuit occurring. The current which flows through the voltmeter, and hence the deflection of the voltmeter, depends on the insulation resistance which is found as follows:

Let a = voltmeter resistance.

Let b = insulation resistance.

Let d = reading of voltmeter in series with insulation with 500 volts across them.

Then the current = $500 \div (a + b)$; but the current also = $d \div a$. Hence $500 \div (a + b) = d \div a$,
 and $\therefore b = a \left(\frac{500 - d}{d} \right) = a \left(\frac{500}{d} - 1 \right)$.

The principal use of the ohmic resistance measurements of insulation lies in the comparison they afford of the damp-proof qualities of various dielectrics, and in the measure of the degree of dryness obtained. This is quite important, because the presence of moisture in almost all the forms of insulation, is a source of great trouble.

TESTS FOR DIELECTRIC STRENGTH

Among the tests which are regularly made to determine the quality of the insulation of a piece of electrical apparatus, is that known as the disruptive or dielectric test.

The following is a discussion of the design, selection and use of apparatus for making such a test. In considering the apparatus, a number of points must be considered.

Maximum Testing Voltage

The maximum testing voltage required depends on the nature of the material or apparatus to be tested. For lower voltage apparatus the testing voltage is usually several times the rated voltage of the apparatus, while for higher voltages, the testing voltage is rarely more than double the normal rated voltage. In the case of materials almost any range may be required from a few hundred volts up to 100,000 or 150,000 volts, so that a well-equipped testing laboratory should be capable of giving this range of voltage. The following table gives a list of the maximum testing voltages suitable for various classes of work, together with the capacity in kilowatts which will be found sufficient for most work for each.

Maximum Testing Voltage	Capacity (kilowatts)		Maximum Testing Voltage	Capacity (Kilowatts)
2,000	1		50,000	50
6,000	3		100,000	100
10,000	5		150,000	150
30,000	30		250,000	250

Frequency of the Testing Circuit

The frequency of the circuit on which the testing transformer is used, determines, in some measure, its size for a given output—the lower the frequency the larger the size. A more important consideration governing the output follows from the fact that the amount of charging current varies directly as the frequency of the testing circuit. So that the higher the frequency the larger must be the testing transformer. Furthermore, the dielectric loss in insulation, at a stress approaching the disruptive strength, also, varies approximately as the frequency, requiring additional testing capacity.

Static Capacity of Apparatus to be Tested

Small samples of insulation require but a very small output in the testing transformer, but with large machinery or with cables, a much larger output is required on account of the current necessary to charge the apparatus considered as a condenser.

Variation of the Testing Voltage

There are three principal methods of varying the testing voltage when making dielectric tests.

- (a) By varying the generator field.
- (b) By means of a resistance in series with either the primary or secondary of the testing transformer.
- (c) Variation by steps.

In the latter method a great range of voltage may be had by bringing out loops from the high tension side of the testing transformer with further combinations of the low-tension windings. Very close regulation of the testing voltage may be obtained by the use of a second transformer. It is connected directly to the line and has a large number of loops in its secondary winding, which are connected through suitable dials to the primary of the testing transformer.

Measurement of the Testing Voltage

(a) By ratio—in the lower voltage work where the static capacity of the apparatus is small the simplest method is to measure the primary voltage and multiply by the ratio of transformation.

(b) By voltmeter reading in the high-tension circuit—a direct reading voltmeter of the current operated type used in series with non-inductive resistance, is used in this method.

(c) By spark-gap in the high tension circuit—this method has been recommended by a committee of the A.I.E.E., with a spark-gap to consist of needles, the distances for the various voltages being given.

(d) By voltmeter and a step-down transformer.

Provision for Locating Faults

In many tests it is desirable to locate the faults which occur during the test. One of the most satisfactory methods is to hold the testing current a sufficient length of time to produce burning of the insulation at the point of fault. For this purpose a resistance or inductance in some part of the circuit is very satisfactory.

Rating of Testing Transformers

The usual method of rating transformers is based on the temperature rise when the transformer is carrying the rated load continuously. As a testing transformer is rarely, if ever, used continuously, it may be rated on the maximum current that the transformer can deliver for short periods of time.

Testing Methods

In the testing of materials, the greatest variety of materials will be met with—as fabrics, porcelain, oil, papers, and almost every conceivable combination of materials.

For sheet material, metal terminals with edges well rounded should be used. For irregular shaped solids, the conditions of service should be simulated as nearly as possible. The method of applying the voltage is not of much importance, whether by steps, by graded rise, or by the application of full voltage at once, where the test is a predetermined amount, and the testing voltage is not high, say not over 25,000 volts.

As the actual breakdown point is desired in most tests on material, the voltage must be applied in pre-determined steps, or the rate of increase must be such that readings may be taken and the exact point of breakdown determined. The voltage may be read by ratio or by a static voltmeter in the high tension circuit.

In the testing of dynamos, motors, transformers, cables, etc., their static capacity must be considered, requiring larger testing apparatus and greater care in the application of testing voltage.

Materials Used for Insulation

Up to the present time the engineer has had to choose his own insulating material from the ones afforded him by the trade. But the materials at hand are not all that could be desired, especially in high tension work, which is greatly handicapped by the lack of suitable insulating materials. Some materials may have one good property in a very marked degree, but at the same time may lack in one or more of the other essentials.

The following is a general idea of the desirable and undesirable qualities of insulating materials, and an indication of some points where improvements might be useful.

(1) Electrical properties.

- a.—Insulation resistance or conductivity expressed in ohms per centimeter.
- b.—Disruptive or dielectric strength, measured by the potential necessary to puncture the material.
- c.—Dielectric constant, or specific inductive capacity in microfarads, or a condenser having a particular material as dielectric separating the metal plates. This last named property is less important than the two preceding.

(2) Mechanical properties.

- a.—Strength and workability, in case of solids.
- b.—Flexibility and workability in case of semi-solids.
- c.—Viscosity, in case of liquids.

(3) Chemical Properties.

- a.—Combustibility.
- b.—Property of resisting the influence of moisture, air, oil, acids, etc.

The factors which may considerably influence the properties of insulating materials during use are the following:

- 1.—Rise of Temperature. It may be due to (a) current passing with not enough chance to radiate the heat generated: (b) Heat conducted into the insulation from outside sources, such as the metallic conductor: (c) Dielectric hysteresis, due to very frequent application and withdrawal of high electric stress, such as high voltage alternating current, with not enough chance to radiate the heat generated.
- 2.—Mechanical stress resulting in change of shape or breaking.
- 3.—Chemical action, as of water, oil, ozone, nitrous fumes (which may be generated by brush discharges) or gases and fumes developed by factory processes in the neighborhood of electrical apparatus.

Desirable qualities are mainly, good insulation resistance, high disruptive strength, and fair mechanical properties, especially workability. Undesirable qualities are, combustibility and changes in electrical and mechanical properties with rise of temperature, or with age, and of course, high price.

To make a chemical classification of insulating materials it is practical to consider them under the heads of:—1. Organic materials, liquids and solids: 2. mixtures of organic and inorganic materials: 3. inorganic materials.

1. (a) Liquid organic materials. These comprise the materials used for transformer insulating and cooling, for condensers and for circuit breakers. Such liquid insulators are the liquid organic compounds.

(b) Organic compounds used as solids of more or less plastic state: These are represented by varnishes, lacquers, drying oils, rubber, and compounds made from the different cellulose materials, such as textile materials, wood, etc. Some of the disadvantages of these as used nowadays are, loss of mechanical strength, insulating power and dielectric strength by age, by high temperature or by high electric stress. All of them are more or less inflammable and some of them, such as gutta percha, are quite expensive.

2. Mixtures of organic and inorganic materials. Typical representatives of this group are materials made of asbestos, or of mica with varnish, rubber or paper. The asbestos compounds, as a rule, lack high insulating power and also mechanical strength. The mica papers lack flexibility and are not apt to be uniform throughout.

3.—Inorganic materials. These are represented by slate, marble, asbestos, porcelain, and glass. They are practically unaffected by heat but lack entirely flexibility and are usually expensive, especially when manufactured into desired shapes.

A comparatively perfect insulation would have the flexibility of rubber and the ideally high insulating and dielectric strength of mica, and should, of course, be cheaper.

Perhaps it would be suitable here to give brief descriptions of some of the more important insulating materials.

Rubber

Para rubber is the name applied to rubber coming from widely different localities, the principal of which are: Brazil, Bolivia and Peru. However, it is not the locality which causes the difference in the paras so much as the methods of gathering and of coagulation. They might be conveniently divided into three grades:—

Fine—The clean and thoroughly cured rubber.

Medium.—In the centre of which there is more or less moisture due to imperfect curing.

Coarse.—The residue scraped from the collecting vessels.

Owing to the ever increasing demand for rubber, the price of para has advanced, and as the supply was inadequate to the demand, the use of rubber other than para became absolutely necessary. Various grades are found in different parts of the tropical world, Africa being the chief source of the better qualities. At first the methods of curing were very crude, but these defects have been largely overcome, so that to-day rubber compounds can be made containing no para, which in almost every respect, will give as good results as the more expensive article.

The most important properties of rubber, considered from the standpoint of insulation, may be grouped under the following heads:

- 1.—Non-hygroscopic.
- 2.—Dielectric.
- 3.—Mechanical strength.
- 4.—Elasticity.

The last three of these properties are materially affected by the process of manufacture, and each one is developed more or less at the expense of the others.

In selecting a rubber compound the manufacturer of insulation carefully considers the following points: First, conditions of service; second, what quality will best meet the conditions with an ample factor of safety and the least cost to the purchasers; third, how in the process of manufacture the most essential qualities of the rubber may be developed so that the resulting compound may be the best possible.

The purchaser of a rubber compound quite naturally submits it to some test which he considers adequate to show in what measure it will meet his requirements. Let us now consider some of these tests.

1.—Acetone Test. In all rubbers there is always a certain amount of oily or resinous matter soluble in heated acetone. Unvulcanized fine para rubber contains from one to two per cent. of this extractive matter, but it has been found that a good compound may contain as much as eight per cent provided it is properly vulcanized.

2.—Ash Test. This is simply the burning up of organic matter in a compound, leaving as ash the inorganic or mineral matter. The amount of rubber in a compound varies considerably: it is seldom less than 30 per cent nor more than 40. The percentage

of ash required must cover such variations. A minimum of approximately 56% and a maximum of 68% would accomplish this.

3.—Stretch Test. Elasticity is the most obvious property of crude rubber, and on this account it has been assumed that good rubber compounds are elastic and that poor ones are not.

Any rubber compound, good or bad, is, at one stage of manufacture, a plastic mass about like putty. Strength and elasticity are given this mass by vulcanization. Precisely the same compound can, by changes in the quantity of sulphur and method of vulcanization, be made highly elastic or as brittle as glass. It has been found that as an insulator the brittle compound is the better from an electrical standpoint, but of course, is useless as a covering for wires and cables. It is obvious, therefore, that the most efficient rubber insulation is that possessing the greatest dielectric and mechanical strength consistent with the retention of sufficient elasticity.

There are good reasons why the Stretch Test should never be applied to insulation on large conductors, or to thick insulation for high pressures, irrespective of the size of the conductor. The mass to be vulcanized on large conductors cannot be done without the sacrifice of elasticity sufficient to make the ordinary stretch test almost impossible. When the outer surface of a thickly insulated conductor has been vulcanized to a point where the elasticity is greatest, the inner layers are under-vulcanized and are therefore highly perishable.

On the smaller sizes and for walls up to one-eighth of an inch thick a stretch test should be useful. The manner of performing it is as follows: a four inch sample is cut from the conductor and marks two inches apart are placed on it, the sample is then stretched until the marks are six inches apart, and on being allowed to return they should be at least two and one-half inches apart. For larger sizes and heavy walls, a sample cut from the conductor the full thickness of the insulation is bent double and the process repeated in reverse. The sample should show no signs of cracking.

4. Insulation Resistance Test. The National Board of Fire Underwriters requires, for a No. 14 B. & S. with 3-64 inch wall of rubber insulation, 200 megohms after 60 hours immersion at 60°F. Telephone companies for the same size and wall of insulation require 500 megs. after 24 hours immersion at 60°F. With the latter as a basis, the insulation resistance for any size of conductor and wall of rubber can be obtained by the use of the formula

$$\text{Constant} = \frac{\text{resistance}}{\log_e (D \div d)}$$

5.—Voltage Test. This is the most important test in determining the practical efficiency of insulation. Excessive voltages should be avoided as they strain the insulation, thereby weakening it and shortening its life. A test of $2\frac{1}{2}$ times the maximum working emf. for 5 minutes after 24 hours immersion, or for twice the maximum working emf. for 30 minutes, will not strain the insulation, but will develop any structural faults and establish the existence of a factor of safety. When the voltage is nominal and the walls of insulation

comparatively thick the working emf. as above would evidently be inadequate. In this case the engineer should determine the maximum emf. which he would be willing to use in the conductor in question, and base the voltage test on this. For example: No. 14 wire with 5-64 inch walls of rubber could safely be used for 2,000 volts of alternating emf., though the actual working stress might be nearly nominal. The test with $2\frac{1}{2}$ as a factor would be 5,000 volts for 5 minutes.

This rule may not be scientifically exact, but it is simple and no insulation successfully tested under it could have either structural faults or inherent weaknesses sufficient to endanger its successful operation. The object of the voltage test should not be to determine the greatest stress to which the insulation can be subjected, but to establish the existence of a safety factor.

Mica

Mica is an anhydrous silicate of aluminium and potassium or sodium. The most transparent qualities are composed of the above mentioned substances, but the less transparent qualities contain magnesia, iron or earthy matter. It crystallizes in layers and may be subdivided down to a thickness of 0.006 mm.

It can safely be said that no satisfactory substitute has been found for mica in commutator construction. The commutator is the hottest part of the machine, and mica will not carbonize.

There are two kinds of mica, amber and white. The amber mica is used between segments, since it can be turned on a lathe better than white. White mica is harder than amber, but much more flexible, and splits into comparatively large sheets which makes it quite applicable to repair work. All variations from white, especially greenish or bluish tinge, are harder and more brittle.

The ultimate disruptive strength of a selected quality of amber mica, taken from a number of samples up to 5 mils in thickness, varied from 1,980 volts per mil to 4,300 volts. The average failing is at about 2,500 volts. The averages of two assortments of poorer grade, mottled samples were 2,200 and 2,400 volts per mil, respectively. White mica, both large and small sheets, averaged 3,100 volts per mil.

The successful building up of thin overlapping sheets and the moulding of finely divided mica into plastic forms, has simplified the insulation of many machine parts. These insulations, known by several trade names, share to a great extent the value of mica. Built-up mica, if cemented with a non-hygroscopic varnish, possesses a disruptive strength practically proportional to its thickness. Backed with a tough paper or cloth, for mechanical strength, it has advantages over pressboard and other fibrous insulations for slot or coil work. The following are a few characteristic built-up mica insulations.

Micanite. In this product the mica is split up into layers and these thin sheets are stuck together by an insulating cement. Natural mica cannot be bent except in a very thin sheet, but micanite,

when heated, may be bent into any suitable form. If the thin sheets are allowed to overlap and a non-hygroscopic cement is used, micanite makes an exceedingly good insulator. It is made in the form of plates, which may be moulded, and also as cloth and paper.

Megohmit. This is similar to micanite. The plates consist of thin mica sheets stuck together with shellac in the case of hard plates, and with a mixture of vegetable adhesive materials, in the case of flexible plates. The megohmit paper consists of flexible plates having a covering of Japanese paper, and megohmit linen is similar except with a covering of linen instead of paper. The hard plates become soft at about 80°C. , but on cooling regain their original mechanical strength. Channel plates and troughs may be made from megohmit plates.

Sheet Insulations

Paper and other fibrous materials are, owing to their close homogeneous texture and even qualities, used to a great extent as insulation. Manilla, express and bond papers probably head the list as far as good disruptive and mechanical strengths are concerned, although the so-called red rope paper is probably most extensively used. These four, when coated with good insulating varnish make excellent dielectrics.

No paper of any kind should be used without first being coated with some moisture proof varnish, because all untreated papers are more or less hygroscopic. Indeed, the present tendency is to abandon reliance upon the insulating properties of these fibrous materials and to depend rather on the films of varnish with which they are coated or impregnated.

One of the most widely used insulations is flexible pressboard. The best quality is made of leather findings and comes in yellow and red. For thicker insulating sheets, preparations of vulcanized or hard fibre are available, including such materials as bone fibre, kartavert, amyloiden, leatheroid.

Hard rubber compounds are sometimes used for sheet insulation, especially those vulcanized with asbestos fibre, but flexibility is, of course, impossible.

Fabrics

At the present time, insulations made of cloths and fabrics are almost indispensable. These serve as a framework to hold the film of insulating varnish, so that their selection is quite important. Cambric, muslin, lonsdale, and batiste are the trade names of the best materials for this purpose. Those materials which have the smoothest surface and are free from nap and fuzz are to be recommended, and for good results the cloth should be first ironed or singed to obtain as smooth a surface as possible; otherwise the nap or fuzz projecting through the film of varnish breaks up the continuity and results in a variable disruptive strength.

There are several different methods of treating cloth with

insulating varnishes. Some require little more than a paint brush and a can of varnish. The cloth is laid on a bench and painted over until the required result is obtained. Another and superior method consists in passing the roll of cloth through a trough containing linseed oil, the cloth having been first dried in an oven. It is again dried and drawn through a vat of varnish which is placed at the bottom of a chimney-like oven. After going through the varnish the roll slowly ascends through the oven and then descends again. The operation being repeated until the coating is sufficient.

Considering the insulations on wires, the materials most commonly used are, cotton, silk, asbestos, and enamel. Cotton must be reinforced with compounds or varnishes to give satisfactory results, and may be used for temperatures below 100°C . Silk is better than cotton in that it takes less space and is only used where a very thin insulation is imperative, owing to its cost.

Although enamel does not come under the head of fabrics, yet it is used to a considerable extent in place of them, so that its discussion is not altogether out of place here.

Enamelled wire is coming into use more and more, and will probably supersede cotton, silk and asbestos. It has a high insulation resistance, is non-hygroscopic, and will withstand a higher temperature than cotton or silk and takes up less room than either. With enamelled wire it is often possible to give a machine a higher rating or to allow for greater overloads, and thus effect a considerable saving in the construction. The danger in enamelled wire lies in its tendency to crack and when bent around small turns, and it also is liable to become brittle.

Oils

It was not until 1859 that oil was used as an insulator, and then it was in connection with submarine cables. As long distance high voltage transmission came to be used, oil insulation was found to be absolutely necessary. Previous to 1890 there had been a limited use of oil for insulating transformers and induction coils, but this was confined to a few of the small sizes and low voltages in transformer work. In 1891 transformers were used, wound for 30,000 volts and having oil as an insulator.

Mineral oil is used universally for this purpose because of its cheapness and general efficiency, and the apparatus is almost always immersed in it. Besides serving as an insulator, oil forms a cooling medium whose function is to receive the heat from the apparatus where it is generated and carry it away. Owing to the fact that oil expands when heated, the hot oil rises and the colder oil from the sides of the containing tank flows in to take its place, thus setting up a circulation of the oil which continually cools the apparatus.

Almost all oils—mineral, vegetable and animal—when pure, are very good insulators. There is a wide difference between the insulating qualities of various mineral oils, but this difference seems to be more an index to the purity of the oil than an inherent difference due to variations in the chemical composition of the oil itself.

By purity is meant freedom from water, alkali, acid or foreign matter of any kind.

Most properties of oils as now used are desirable, but one bad feature inherent in them is their combustibility. In the case of circuit breakers as well as of transformers, where accidental high potential may have arced through the oil, the broken down insulation should soon repair itself and the oil should soon come back to its original insulating power. Besides this, oils should be considered as to their effect on the different materials they come in contact with. For instance, fatty acids are undesirable because they are apt to react with copper. Then, too, the products resulting when the discharge goes through, should not be such as to injure any part of the apparatus.

Methods of Testing Oil Insulation

(a) The method usually employed in determining the insulating value of an oil is to test its dielectric strength. Satisfactory insulation resistance tests are difficult to make and, while showing something of the quality of the oil, are not of as much value as dielectric tests.

The usual method is to immerse spark gaps in the oil, the gap being set at a known distance, and gradually rising the potential until rupture occurs.

(b) Another important test is the "flash and fire" test. By flash test is meant the temperature to which oil must be heated in order to give off gases which burn when ignited and which form explosive mixtures with the air. By fire test is meant the temperature to which oil must be heated so that the oil itself will take fire, and continue burning when a flame is applied to its surface. The general method is to heat the oil gradually, applying a test flame at intervals, and noting the temperature at which a slight flash occurs, and also the temperature at which the gases take fire and continue burning.

(c) Moisture. The deteriorating effect of moisture on the insulating value of an oil is very marked. As there are many ways in which moisture may enter the oil, tests for moisture become very important.

The test consists in placing a small amount of oil in a cup, into which is plunged a piece of iron or other metal, at a temperature just below a dull red heat. Any hissing or crackling noise indicates the presence of moisture.

Specifications

The following is a brief specification for insulating oil:

(1) The oil should be a pure mineral oil obtained by fractional distillation of petroleum unmixed with any other substance and without subsequent chemical treatment.

(2) The flash test of the oil should not be less than 180°C., and the burning test not less than 200°C.

(3) The oil must not contain moisture, alkali, or sulphur compounds.

(4) It should not show an evaporation of more than 0.2% when heated at 100°C. for 8 hours.

(5) It is desirable that it should be as fluid as possible, and that the color be as light as can be obtained in an untreated oil.

Insulating Varnishes and Paints

Insulating varnishes are employed to improve the initial insulating properties of papers, fabrics, and fibrous materials, which are impregnated with them, and to maintain the constancy of their initial insulation resistance.

An insulating varnish should give a permanent uniform coating of insulation which will not become brittle, crack, or peel off. It should be plastic and should not flow below 200°C. It should not cause corrosion and neither water, acids nor oils should affect it, and it should be cheap.

(Varnished cloth and paper are now used universally, but the day of the simple gum varnish is past. It has been found that insulation dipped in a hot bath of copal gum or shellac would "check" when chilled and tend to crumble away under vibration. Moisture soon finds its way into the minute cracks, and destroys the insulating value. These gum varnishes must also be dissolved in alcohol, naphtha, or some highly volatile liquid, and the result is that there is danger of fire, as well as waste owing to evaporation. Asphalt, bitumen and other mineral patches have faults similar to gum varnishes. Linseed oil, when thoroughly boiled out, has been combined in many successful varnishes, but after the lapse of time it has a tendency to oxidize and crack).

The following are a few of the better class of these varnishes:

(1) Sterling Insulating Varnishes.

These are composed mainly of linseed oil, turpentine and resin. They have a high uniform insulation strength and are claimed to be impervious to the action of water and oil. They are generally applied to fabrics of paper, which are given a thin coat and afterwards baked in an oven at from 60° to 80°C.

Other Sterling products are:—Sterling Quick-Drying Insulating Varnish; Elastic Insulating Varnish; Black Plastic Insulation.

(2) Armalac.

A fault sometimes found with linseed oil varnishes is that the acid in the oil corrodes the copper of the windings. Another fault is that lubricating oil acts on the linseed oil and upon insulations impregnated with these varnishes.

Another class of varnish has been brought out which overcomes these faults. A typical one of this class is Armalac, which is composed of black paraffin wax dissolved in petroleum naphtha, the melting point of the paraffin being permanently raised by a secret process. It is claimed that although its melting point is about 300°C., it never becomes hard or brittle, that there is an entire absence of resin acids and that it does not affect copper.

No varnish is suitable for all purposes. A varnish which corrodes may be used, provided another varnish which does not do so is applied next to that copper. A varnish which remains soft and pliable is best for form wound armature coils, as flexibility is essential in assembling and repairing them. In some cases a varnish need not have high insulating properties, if only it is tough and durable. For some purposes a varnish must dry quickly in air and have a hard smooth surface. In some cases a waterproof varnish is necessary, and again it may have to resist acid fumes or heat.

(3) Benolite.

A new varnish has come out under the name of Benolite. It is a black, waterproof, oil-proof, flexible varnish, which can be dried in air in from four to six hours, the drying being caused by chemical action other than by oxidation, and stopping at a point which leaves the varnish quite flexible. Once dry, Benolite is absolutely acid and alkali-proof, the finish not only being unaffected itself, but protecting the copper or cloth underneath from corrosive action.

A single layer of cotton tape painted with Benolite is stated to have a dielectric strength of from 6 to 10 thousand volts. A superior insulation can be obtained by taping the article with cotton or linen tape, painting four or five times the Benolite and drying each coat for about two hours. The Benolite thoroughly penetrates the tape and forms a fine glossy surface. The result is a thoroughly dry homogenous mass of insulation having a high dielectric strength. The fact that it dries by chemical action makes it unnecessary to be in contact with the air to dry, and its penetrating and flexible qualities make it an excellent material for this kind of work.

Special Insulations

Some of these have already been referred to, but there are a number which do not come under any of the foregoing heads.

(1) Asbestos Insulation.

Of late years there has been a tendency to use fireproof insulation on cars, and it is becoming more general on account of the recommendations of the Board of Underwriters, which require under-frames to be covered with a fire-proof insulating material.

Two new materials have lately been brought out, called asbestos building lumber and magnesia building lumber. The former is composed of asbestos fibre, each fibre being coated with a cement, and these coated fibres then united by a peculiar process giving a substance of fibre-like construction, which under great pressure can be moulded to any shape. The other material is made up of the natural fibres of magnesium silicate cemented together by the use of an artificial magnesium silicate, which is crystallized around them. It may be moulded also, and both materials may be cut and sawn, and in fact used in a similar way to ordinary wood.

Tests for insulation resistance were made at 550 volts, showing the following results:—

ASBESTOS LUMBER

Thickness	Resistance per inch of Thickness
1-8 inch.	0.97 to 2.3 megohms
¼ inch.	0.2 to 1.2 megohms
½ inch.	0.8 to 1.5 megohms

MAGNESIA LUMBER

Thickness	Resistance per inch of Thickness
1-8 inch.	1.3 to 8.7 megohms
¼ inch.	1.05 to 4.1 megohms
½ inch.	1.09 to 3.5 megohms

The break-down voltage test was made upon specimens of both materials, dried five hours at 150°C., and also upon undried specimens. In the Asbestos Lumber the results showed breakdown voltages of from 7,000 to 21,000 volts per inch of thickness, while when undried they were from 2,700 to 12,000 volts per inch of thickness. In dried magnesia lumber the break-down voltages varied from 9,000 to 30,000 volts per inch of thickness and in undried material it was from 4,800 to 15,000 volts per inch of thickness.

The absorption tests tended to indicate that both materials absorb a certain amount of moisture, the magnesia lumber showing the greater tendency in this direction.

As a result of tests for strength, it was concluded that of the two, asbestos lumber possessed better mechanical properties than magnesia although the latter is a better electrical insulator.

One of the chief uses to which the material is being put is for insulating and fire-proofing the lower parts of cars, the lumber being painted with moisture proof paint.

(2) Bakelite.

The Bakelite Co. is the manufacturer of a product possessing valuable characteristics for insulating purposes, called "Bakelite." It possesses some of the combined properties of amber, hard rubber and celluloid, but it is harder and stronger than any of them, withstands heat and is not attacked by any solvents nor by most chemicals. The substance is totally insoluble and infusible, and does not soften even at a temperature of 572°F. It may be obtained either transparent or opaque, and can be compounded with various filling materials, such as asbestos, clay, wood pulp, minerals, etc., and shaped or moulded to articles of unusual strength. It can be sawed, polished, and turned, and when used to impregnate wood and other porous bodies, renders them harder and more resisting to chemical and physical influences. The material does not emanate sulphur, like hard rubber, nor nitrous products like celluloid, and if heated it does not catch fire nor melt, but simply chars and then burns with difficulty. The various forms of "Bakelite" are applicable to such a variety of purposes that it is necessary to specify what use is intended in order to obtain the proper variety.

(3) Insulation by Freezing.

A rather unusual line of investigation has been taken up by Mr. Tesla, namely, that of insulation by freezing. Long ago Faraday estimated that water and aqueous solutions insulate a hundred times better if frozen solid. Tesla has confirmed this, and in the course of his experiments has ascertained the following points:

(1) Under certain conditions, where the leakage of the electric charge

ordinarily taking place is rigorously prevented, ice proves itself to be a much better insulator than has heretofore appeared. (2) That there is benefit in adding other bodies to the water. (3) That the dielectric strength of ice increases with the reduction of temperature. (4) That there is most gain in regard to alternating currents at high rates, very thin slices of ice being capable of enduring electromotive forces even into thousands of volts. Upon this and other data he has made some ingenious applications, as shown in his patents.

In carrying out his methods he uses a hollow conductor and passes the cooling agent through it or he uses expressly for the circulation of the cooling agent an independent channel, and freezes the adjacent substance in which the conductors lie. Another plan illustrates a method of immersing the primary and secondary of transformers in a freezing jar.

(4) Electrore.

About eighteen years ago there was developed and placed on the market a form of insulating composition possessing many unusual characteristics. Although the material was non-fireproof, yet it was found to be well adapted to high voltage work, and capable of withstanding arcing without destruction. Beginning in 1902, the material was used for high tension line insulators on the circuits of the Niagara Falls Power Company and the Canadian Niagara Power Company. It is claimed that, although lightning has frequently caused arcs to form around the insulators, not one has been damaged by it. This result is attributed to inherent flexibility of the material, which permits it to withstand heat expansion strains which would immediately rupture either glass or porcelain.

The material which is called "Electrore," possesses hardness, and toughness without brittleness, great strength, a smooth polished surface, and is moisture, water and oil proof. It will not shrink, warp or change its form under ordinary conditions, and is suitable for use in temperatures below 200°F.

The following tests illustrate some of its characteristics: a sheet 12 inches by one-eighth inch arced around at 75,000 volts but did not puncture: a similar sheet $\frac{1}{4}$ inch thick withstood 80,000 volts without puncturing: a corrugated rod type insulator 7 inches long by 15 inches in diameter arced over from terminal to terminal at 80,000 volts, but did not puncture.

Energy Losses in Insulation

In experiments to test the dielectric strength of insulating materials by means of alternating emf., it is a noticeable fact that heat is always developed in these materials. When the amount of material involved is large, ordinary instruments will show an actual loss of energy.

The materials used in the test were of a fibrous nature, such as paper or cloth, both treated and untreated, and a great many tests had to be made in order to arrive at reliable results. Tests were also made on finished apparatus. Alternating current at the

standard frequencies of 25, 60 and 125 cycles was used, with emf. varying from a few thousand volts up to 100,000 volts. The results, while true for all potential stresses, are of little importance in ordinary low potential apparatus, but become of great importance in very high potential working. The results have also a direct bearing on questions of long continued tests of dielectric strength of finished apparatus at very high voltages.

The loss above mentioned has been found to depend on (1) temperature, and (2) frequency, and temperature changes with the voltage.

Variation of Temperature Due to Variation of Stress

The following are the results of a series of tests on insulating materials:

(1) With moderate stress the temperature rises at first rapidly, then more slowly, then becomes constant.

(2) As the stress is increased, a point is reached where the heat is developed faster than it can be carried away and the temperature rises until the material chars and breaks down.

(3) When material is not well dried, the temperature rise much more rapidly than in well dried stock.

(4) The final break-down in fibrous materials usually results from the burning of material and not from mechanical rupture.

(5) It follows from (4) that if the temperature is kept low, the stress required to cause break-down will be much greater than if the material is not so cooled.

(6) With a given stress, the initial and surrounding temperature has much to do with the rise. The higher the initial temperature, the greater the rise.

Variation of Loss Due to Variation of Temperature

The following points were brought out in experiments to ascertain the loss due to variation of temperature.

(1) The energy loss in fibrous materials increased with temperature.

(2) The ratio of increase in the loss depends on the kind of material and its condition.

(3) The local heating found in a mass of poorly ventilated material is due to a greater initial loss in one portion causing increased heating, this in turn causing greater loss, etc., until the material breaks down.

(4) The rate of increase of loss is greater at high than at low temperatures.

(5) A long continued test at high stress may seriously injure the insulation of a piece of apparatus, without this being made apparent by the test.

Variation of Loss Due to Variation of Voltage

The results of a great many experiments show the following, with constant temperatures:

- (1) The increase in loss is usually slightly greater than the square of the emf.
- (2) With varying temperature the loss will increase more rapidly than the square of the voltage.
- (3) The rate of increase will depend on the facility with which the material can get rid of its heat.
- (4) It will also depend on the initial temperature.

Energy Loss in the Insulation of Large Alternators

From tests made on two 5,000 k.w. alternators, at approximately 5,000, 10,000, 15,000 and 20,000 volts, the following conclusions were arrived at:

- (1) The variation in loss due to change of stress is slightly greater than the square of the applied stress.
- (2) There was a great increase in the loss for the higher temperature.
- (3) The loss at 25,000 volts is not sufficient to cause any injurious heating.
- (4) The rate of increase of loss shows that above 25,000 volts the loss would be sufficient to cause heating and damage to the insulation, if the stress were applied for any considerable time.

Selection of Machine Insulation

Materials intended for the insulation of electric machinery should pass three classes of requirements involving tests to withstand (1) Current Leakage, (2) Lightning Discharge, (3) Heat.

Number 1 includes not only actual insulation resistance tests under any set of conditions measured in megohms, but also hygroscopic tests which affect the insulation resistance of many porous materials. Number 2 includes the determination of the resistance due to disruptive discharge from any cause, whether accidental metallic contact with a high-tension line wire, proximity to high frequency wireless station apparatus or static discharge during a thunderstorm. Under number 3 is included tests covering the effects due to the presence or absence of heat, such as the mechanical failure of materials with extremes of temperature or with rapid alternation of heat and cold.

No station leading from an overhead line can be absolutely protected from lightning discharge, and it frequently happens that the high-potential strain from this cause reaches the insulation of machines. Disruptive discharge of any kind acts like a fluid in motion with erratic splashings which have been called side flashes. These uncontrolled discharges have been found to strain and break down the insulation at any point, but are most liable to follow surface leakage, as in tapped windings, or over a moisture soaked varnish. Discharges will leap over such surfaces and cause short-

circuits and grounds by the secondary effect of the following dynamo current in burning out the machine insulation. Designers, therefore, as far as possible, allow large margins of safety in the actual disruptive strength of the insulating layers.

In some cases the design of the machine will allow of the use of a considerable thickness of insulation resistance, but quite often only thin layers can be used. Tests must be made on different thicknesses of material and on a great variety of materials. It might appear easy to tabulate a set of results and adhere to it in practice, but from a single sample, a great variety of results may be obtained according to the conditions under which the test is made.

BOOK REVIEW

"The Clay and Shale Deposits of the Western Provinces" is the subject of a preliminary report by Heinrich Ries and Joseph Keele, '93, of the Geological Survey Branch, Department of Mines, Ottawa. The report is based on a season's investigations in the field, followed by a long series of laboratory work. It includes a summary of the existing conditions throughout the great western region, and contains a wealth of knowledge covering the many varieties of shales and clays included in the area. It emphasizes the advisability of the development of the clay industries, including paving, fire and common brick, drain tile and sewer pipe. The results of tests made upon numerous samples should be of interest to manufacturers. Analyses are given of clays from various points in Manitoba, Saskatchewan and Alberta, and valuable statistics regarding the formations of sandstone and shale in both the prairie and mountain regions also appear.

The report contains an account of the present state of the clay industry in the West, the brick plants in Winnipeg, Victoria and Vancouver; fire clay in Clayburn, B.C., and sewer pipe in Medicine Hat. It presents the total value of all clay products of the Western provinces for the years '07, '08 and '09, to be as follows:

	1907	1908	1909
Manitoba.....	\$466,432	\$265,091	\$599,008
Saskatchewan.....	125,459	187,566	145,516
Alberta.....	353,672	240,384	442,486
British Columbia.....	306,137	344,446	470,442

The unparalleled demand of the present season is expected to be a great stimulus to the clay working industry.

The volume closes with chapters explaining methods of testing clays and a valuable treatise dealing with the nature and classification of clays. The report is supplemented by over sixty plates and maps.

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EDITORIAL

The announcement has recently been made of the establishment of a University degree of Bachelor of Science in Agriculture. It may be conferred upon candidates who have completed a course extending over two years at the University and two years at the Agricultural College. One year's further

AN OLD QUESTION training in the Faculty of Education leads to a specialist's certificate entitling the holder to teach both Science and Agriculture in a High School.

There are two classes of professional High School certificates: the assistants' and specialists'. The specialists' are issued only to the holders of the assistants'. All specialists are supposed to possess the academic standing in the general subjects required of those who hold an assistant's certificate. This academic standing is what has heretofore been a standard of admission in the Faculty of Education.

The degree of B.A.Sc., is inferior to the degree of B.A. in the matter of English, History, Latin, French, Greek, etc., and has not been recognized, therefore, of sufficient academic standing for a High School assistant's or specialist's certificate; and our graduates could not hope to obtain a teacher's certificate of either grade in the Faculty of Education.

Three years ago the Engineering Alumni Association took up the matter with the Superintendent of Education, and received a very unsatisfactory reply, in so far as the School man is concerned. The B.A.Sc. standard was not sufficient, and furthermore there was little or no demand in the High Schools for teachers of courses of instruction on subjects taught in the Faculty of Applied Science.

Since that time the interests of technical education have grown to demand instructors equipped with a knowledge of the various branches of engineering and of architecture. As an example, the Haileybury High School is searching for an instructor to take charge of a course of study in mining. Sudbury already has such a department in its High School. Substantial government aid is tendered these departments under a clause of the act entitling grants to industrial and agricultural departments of High Schools. The two examples of the new branch mentioned above command respectable remuneration. As technical education broadens its scope, Ontario and the other provinces will require similar officials in almost every High School with, it is to be hoped, similar salaries attached.

Viewing it from the School man's side, the graduating class yearly includes men who have a natural talent for teaching, and to whom such a field would be of interest. It is regrettable that the degree of B.A.Sc. is not considered tantamount with other degrees entitling the holders to admission to the Faculty of Education, so that he may receive the finishing touches prior to entering upon such work. The degree of B.A.Sc., however, is yearly spanning the gap between it and the entrance requirements mentioned above. It is now time for the Department of Education to examine the requirements and character of this degree, and for the graduates in Applied Science to agitate the reasonable reforms imp'ied, not merely for their own advantage, but in the interests of the future which we look upon technical education to make for industry in general.

The research scholarship committee of the University of Toronto Engineering Alumni Association has made two awards. This

SCHOLARSHIPS

has been done after numerous meetings for the consideration of applications, discussions of subjects, of their importance and of their suitability to the equipment, resources and time, that may be consigned to them. The selection now awaits the sanction of the faculty committee appointed to consider these scholarships, and of which the Dean is chairman. It is expected that the fellows will be at work by the opening of the term. They are both at hand and are making all preliminary preparations.

The awards were made to M. R. Shaw, '09, and W. P. Dobson, '10. These men, it will be remembered, were favorably considered last year, but were not donated scholarships, Mr. Shaw not having then had the advantages of a fourth year training, which he now possesses, and Mr. Dobson's subject, last year, although being timely and extremely important, not lending itself to the possibilities for the diligent research that would insure progress with the laboratory means at hand.

Mr. Shaw is a graduate in chemical engineering and has already been engaged in research work on various occasions. He was for a time in the employ of the Dow Chemical Co., of Midland, Mich., as chief assistant research chemist, and also with the Imperial Oil Co., of Sarnia, in like capacity. His thesis for the degree of B.A.Sc. last year was based upon, "The Substitution of Pure Oil for Linseed Oil in Paints." In his new undertaking as our research scholar he will confine his efforts to an investigation of the deodorization of the pine distillate that comes over after the extraction of turpentine. It is probable that a careful treatment of the subject will result in information of particular value. In the past years the price of turpentine, the chief and most important of the distillates, has decreased in commercial value to such an extent that a field for the various other distillates must enlarge correspondingly, thus increasing their value as commodities, so as to enable the producing plants to still carry on operations profitably.

Mr. Dobson will make an oscillographic investigation of the line disturbances due to switching on and off heavy loads in high tension systems. Since graduation he has been in the employ of the Toronto Hydro Electric System, and is familiar with the conditions governing, and peculiarities invading, high tension operation. During his course in electrical engineering, his summers were spent on the design and operation of higher voltage apparatus.

His subject is one that is ripe for diligent examination. But little has heretofore been accomplished in an experimental way, and nothing at all has been done by way of investigating conditions on the particular lines carrying current at the extremely high pressures to which they are subjected in the transmission of power from Niagara to Toronto. It is upon these lines that Mr. Dobson proposes to work. He will endeavor to obtain more accurate and detailed information than is now available regarding the oscillations which are produced when large amounts of power are switched on and off a transmission or distribution circuit. His task will include a study of the effects of switching in upon the line various classes of machinery, his aim being to lessen the difficulties of operation and liabilities to interruption of service. Any unusual phenomena, e.g., line surges, lightning, etc., will probably be investigated. At any rate the subject affords Mr. Dobson ample opportunity for intimate acquaintance with the product of the "White Coal."

BOOK REVIEW

Primer of Scientific Management, by Frank B. Gilbreth. Published by D. Van Nostrand Company, New York; cloth, size 5" x 7½" 108 pages.

Those interested in scientific management and its many applications, and especially those who were fortunate enough to hear Mr. Gilbreth on "The Place of Motion Study in Scientific Management," in Convocation Hall, last March, will read with renewed interest his latest book on the subject. As the name suggests, it is an elementary treatment, the author imparting his information in the form of answers to questions. One enquiry, with its complete answer, follows its logical precedent, leading through an easily understood elucidation of the principles and their applications, the effect of scientific management on the workman himself, and the relation of the problem to other lines of activity.

The book will be of great assistance to managers, superintendents and foremen, who have realized that scientific management really secures greater production for the same or less effort, and who are endeavoring to introduce it into their business. It will be of greatest assistance, however, to those who are dubious concerning the movement, by removing from their minds all misapprehensions and suspicions that may have been caused by a study of the complex treatment given the subject in many comments by the technical press.

The engineer and the contractor do themselves injustices in being of the opinion that scientific management is for the manufacturer to consider and that little improvement need be expected in its application to engineering work. Every man who handles workmen, and every workman, as well, should be interested in the movement which aims at "square deal" and co-operation between workman and employer. The opening paragraph of Mr. Gilbreth's new book quotes Dr. Frederick W. Taylor thus: "The principal object of management should be to secure the maximum prosperity for the employer coupled with the maximum prosperity for each employee."

ERRATA

Referring to the examples of architectural design in the August number of APPLIED SCIENCE, the illustration described as a "Legislative Building for a Canadian Province" by J. H. Craig, and another termed "Design for Parliament Buildings" by H. H. Madill, were both mis-named. Each represents a design for a casino.

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